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FOR
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**Kinetic and Modeling Investigation on Dilute-Acid Pretreatment of Hardwood,
Hardwood Bark, and Corn Cobs/Stover Mixture Feedstocks**

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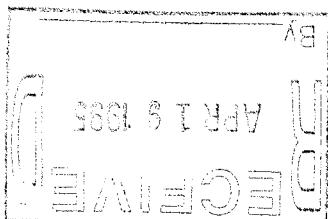
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TASK 1. Kinetics of Dilute Acid Pretreatment of Hybrid Poplar Bark

The kinetic study for the pretreatment of Hybrid Poplar Bark (HPB) was carried out. The kinetics were modeled by hydrolysis of hemicellulose, followed by hydrolysis of oligomer, then decomposition of monomeric sugar. The kinetic parameters were determined from experimental data covering conditions of temperature of 140-170 °C, sulfuric acid concentration of 0.42 - 1.87% (corrected by the biomass buffer capacity), and liquid:solid ratio of 11.3:1.

EXPERIMENTAL METHODS

1. Sample Preparation

HPB was supplied in the form of fine particles by NREL. The feedstock analysis was conducted following the NREL CAT Standard Procedures ^[1,2,3,5,6]. The results are shown in Table 1.

Table 1. Properties of Hybrid Poplar Bark

Sugar:	[gram of sugar / gram of biomass (dry)]x100
Glucan:	30.3
Xylan:	11.2
Araban:	1.89
Galactan:	1.97
Mannan:	1.04
Lignin:	
Klason:	31.84 [gram of lignin / gram of biomass (dry)]x100
Acid Soluble:	2.31
Ash:	7.80
Moisture:	10.40 [gram of water / gram of biomass (dry)]x100
Buffer Capacity ^a :	8.12 [mg of sulfuric acid / g. of biomass (dry)]x100

a: The buffer capacity of biomass was measured by titration method.

The buffer capacity in HPB was determined to be 8.12 mg(sulfuric acid)/g biomass(dry). The acid concentration initially charged into the reactor were corrected accordingly, such that the four levels of acid concentrations of 0.49, 0.74, 1.22, and 1.95 wt% respectively were recalculated to be 0.42, 0.66, 1.14, 1.87 wt% respectively. The corrected values were applied in the kinetic study.

2. Batch Reactions

Reactions were carried out using pyrex glass tube reactors (11 mm i.d.). Glass tubes were packed with 0.5 g biomass and 5 ml acid solution, and sealed at both ends under natural gas - oxygen flame. To initial the reaction, the glass reactor ampules were placed into an oil bath (HAAKE FS2 model) in which the temperature was preadjusted to a temperature 50 °C higher than the desired reaction temperature. After 50 seconds, the ampules were transferred into another oil bath preset at the desired reaction temperature. The temperature measurement within the reactor has shown that the center section of the reactor reached the set point in 50 seconds. Temperature was measured by a thermocouple thermometer. The two oil bath procedure was done to minimize the preheating time. The time when the glass ampule was put into the second oil bath was set as the zero point of the reaction time. After being subjected to specified reaction times, the reactors were quenched in a cold water bath.

3. Analysis

Analyses for solid samples were performed by HPLC(Water Associate) using RI detector and a Bio-Rad's Aminex HPX-87P column. The column temperature was set at 85 °C and the mobile phase flow rate was set at 0.6 ml/min. The liquid samples were analyzed by HPLC using RI detector and a Bio-Rad's Aminex HPX-87C column with column temperature at 85 °C and mobile phase of water at flow rate of 0.6 ml/min.

The kinetic data analysis was done on the basis of XMG_ose (xylose+mannose+galactose) equivalent. During the experimental work, we simplified the work by considering XMG_an (xylan+mannan+galactan) and XMG_ose oligomer (xylose oligomer + galactose oligomer + mannose oligomer) as one complex, then, the concentration of the complex = initial XMG_an - XMG_ose - decomposed products (DP). Since DP was much lower than other components, it was then neglected. In expressing XMG_an content, a weight gain factor for water addition in hydrolysis ($[150/132*11.2+180/162*(1.97+1.04)]/[11.2+1.97+1.04] = 1.13$) was multiplied. For example, a sample containing 1 g XMG_an/100 mL was expressed as 1.12 g XMG_an as XMG_ose/100 mL.

4. Kinetic Models

From our preliminary work, as shown in Figure 1, it was concluded that it would be appropriate to adopt the concept of monophasic hemicellulose such that:

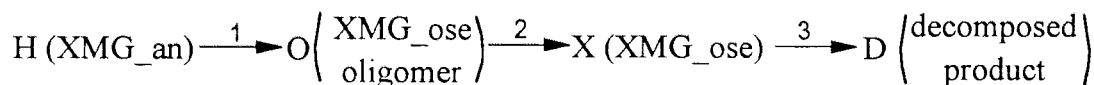


Figure 1. Acid Hydrolysis Pathway of HPB Hemicellulose

We have found that the XMG_ose oligomer is difficult to determine since the oligomer of XMG_ose and glucose oligomer overlap in the HPLC chromatogram. We also found that the presence of oligomer is significant only at the early phase of the reaction, and its level has decreased as the reaction proceeded and eventually disappeared towards the end of the reaction. On the basis of these observation, we have simplified the above reaction pattern by combining two components (XMG_an and XMG_ose oligomer, which concentrations were unable to be determined) as one complex component, HO, as shown in Figure 2.

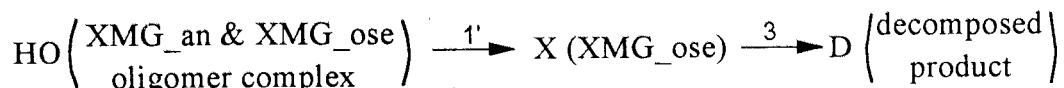


Figure 2. Simplified Acid Hydrolysis Pathway of HPB Hemicellulose

For the proposed kinetic model, the variation of individual component can be theoretically determined by the following set of differential equations:

$$\frac{dX}{dt} = k'_1 A^n HO - k_3 AX \quad (1)$$

$$\frac{dHO}{dt} = -k'_1 A^n HO \quad (2)$$

with initial conditions:

$$\begin{aligned} t=0, \quad HO &= H_0, \text{ and} \\ t=0, \quad X &= 0. \end{aligned}$$

From equations (1) and (2), one obtains:

$$X = \frac{H_o k_1' A^n}{k_3 A - k_1' A^n} (e^{-k_1' A^n t} - e^{-k_3 A t}) \quad (3)$$

To determine the kinetics parameters in equation (3), a SAS NLIN Program was employed to regress the above objective function.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Selection of Reaction Conditions

In order to verify the kinetics of hemicellulose hydrolysis, batch experiments were conducted according to the procedure previously described. After reviewing the results of preliminary runs, the experimental conditions were set to cover 0.49 - 1.95 wt% (without correction for biomass buffer capacity) sulfuric acid and 140 - 170 °C reaction temperature. To ensure uniform wetting condition of HPB, we have applied the L/S ratio of 11.3:1 in the glass ampule reactor experiments.

2. Determination of Model Parameters

The results of XMG_an hydrolysis in HPB are shown in Figure 3. The residual complex (XMG_an + XMG_ose oligomer) concentration were plotted against reaction time for various conditions. The straight lines in the semi-log plot indeed confirmed that the XMG_an in HPB can be considered as monophasic. Thus, for modeling purpose, equations (3) becomes suitable to represent the relations of change of XMG_ose concentration with time.

In the modeling procedure, the experimental data at 140, 150, 160 and 170 °C were fit into equation (3). The k_3 data were extrapolated from the work of Kim and Lee^[4]. During the regression (see program in Appendix 1.), the best fitting n value was found to be 1.4 as shown in Table 2. The remaining four parameters (k_1 at four different temperature level) were determined employing data from 17 experimental runs. The parameter estimation was performed by a nonlinear regression analysis. The resulting kinetic parameters are shown in Table 3. The statistical analysis has shown the upper limit of the standard deviations of the kinetic parameters was less than 6% (see Appendix 2, "Modelling Results of Hybrid Poplar Bark Hydrolysis").

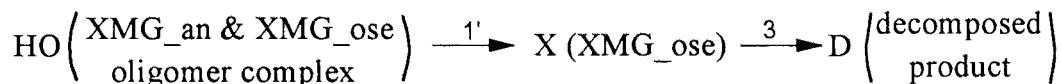
Figure 4 shows that the resulting kinetic data for k_1 is in good agreement with Arrhenius equation. Table 4 is the activation energies for reaction 1' and 3. Of particular significance is that reaction 1', XMG_ose formation, is less sensitive to temperature than reaction 3, XMG_ose

decomposition, but it is more sensitive to acid concentration than reaction 3. Thus, the lower the temperature and the higher the acid concentration, the higher the yield of XMG_ose is expected. Our experimental results bears this assertion. As shown in Figure 5, in all cases, the optimum yield of XMG_ose formation increases with increasing acid concentration. The optimum time decreases with increasing acid concentration. High acid concentration is recommended by the kinetic model. Generally, the yield was seen to decrease at higher temperature, with one exception that at 150 °C, the yield is slightly lower than that at 160 °C. The reaction time to reach the maximum yield at 150 °C is much longer than the one at 160 °C.

The comparison between the predicted reaction progress calculated from the model and associated parameters and the actual experimental data are shown in Appendix 3("Comparison Between Experimental and Model Values for Reaction Progression in Hydrolysis of Hybrid Poplar Bark"). The model prediction is in good agreement with experimental data, thus confirming that the proposed model and the associated kinetic parameters are valid for hydrolysis of Hybrid Poplar Bark hemicellulose.

SUMMARY

1. The kinetic pattern of dilute acid pretreatment of HPB can be modelled as two step series:



2. Hemicellulose in HPB is of monophasic.
3. XMG_ose formation is less sensitive to temperature than XMG_ose decomposition.
4. XMG_ose formation is more sensitive to acid concentration than XMG_ose decomposition.
5. High acid concentration is recommended to obtain high yield of XMG_ose formation and short reaction time.
7. The reaction temperature of 160 °C is considered to be a near optimum reaction condition as it gives relatively high yield and reasonably short reaction time.
8. The model prediction is in good agreement with experimental data.
9. The proposed model and the associated kinetic parameters are valid for hydrolysis of HPB hemicellulose.

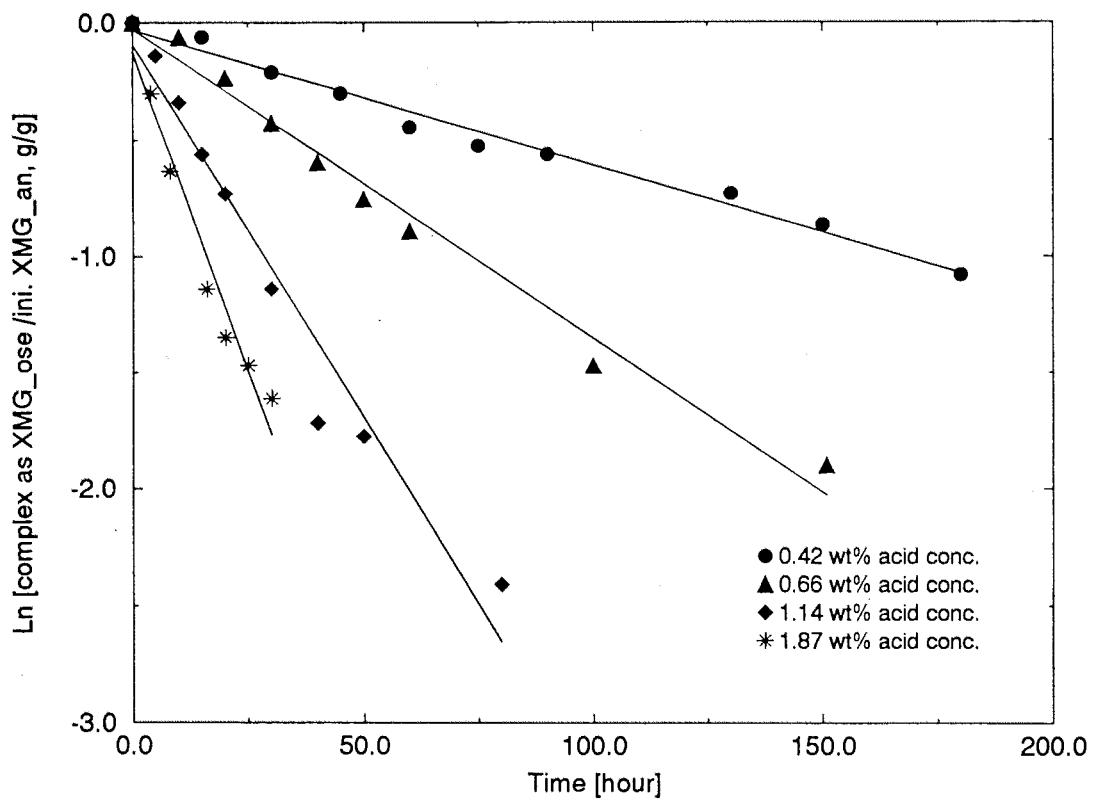


Figure 3. Decay of XMG_an and XMG_ose Oligomer Complex Content in HPB Hemicellulose during Hydrolysis
(Temperature=140 °C, Solid:Liquid=1:11.3)

Table 2. Determination of the Best Fitting n Value

n value	E ₁ sum of square for 140 °C	E ₂ sum of square for 150 °C	E ₃ sum of square for 160 °C	E ₄ sum of square for 170 °C	Sum of E ₁ to E ₄
1.0	0.826	0.780	0.507	0.617	2.73
1.1	0.620	0.620	0.475	0.538	2.25
1.2	0.452	0.483	0.474	0.494	1.90
1.3	0.320	0.383	0.503	0.487	1.69
1.4	0.230	0.314	0.560	0.514	1.62
1.5	0.178	0.277	0.650	0.575	1.68
1.6	0.158	0.270	0.774	0.667	1.87

Table 3. Kinetic Parameters from Modeling^a

Temperature (°C)	140	150	160	170
$k'_1 [\text{min}^{-1}(\text{wt \%})^{-1.4}]$	0.0277	0.0510	0.1123	0.1645
$k_3 [\text{min}^{-1}(\text{wt \%})]$	0.00130	0.00292	0.00630	0.01315

a: n=1.4.

b: After Kim and Lee⁽⁴⁾

Table 4. Activation Energy for Each Reactions.

k_i	k_{oi} [$\text{min}^{-1}(\% \text{w/w})^{-ni}$]	n_i	E_i [kcal/g mol]
I'	1.84×10^{10}	1.4	22.3
3^a	8.99×10^{11}	1.0	28.2

a: After Kim and Lee⁽⁴⁾

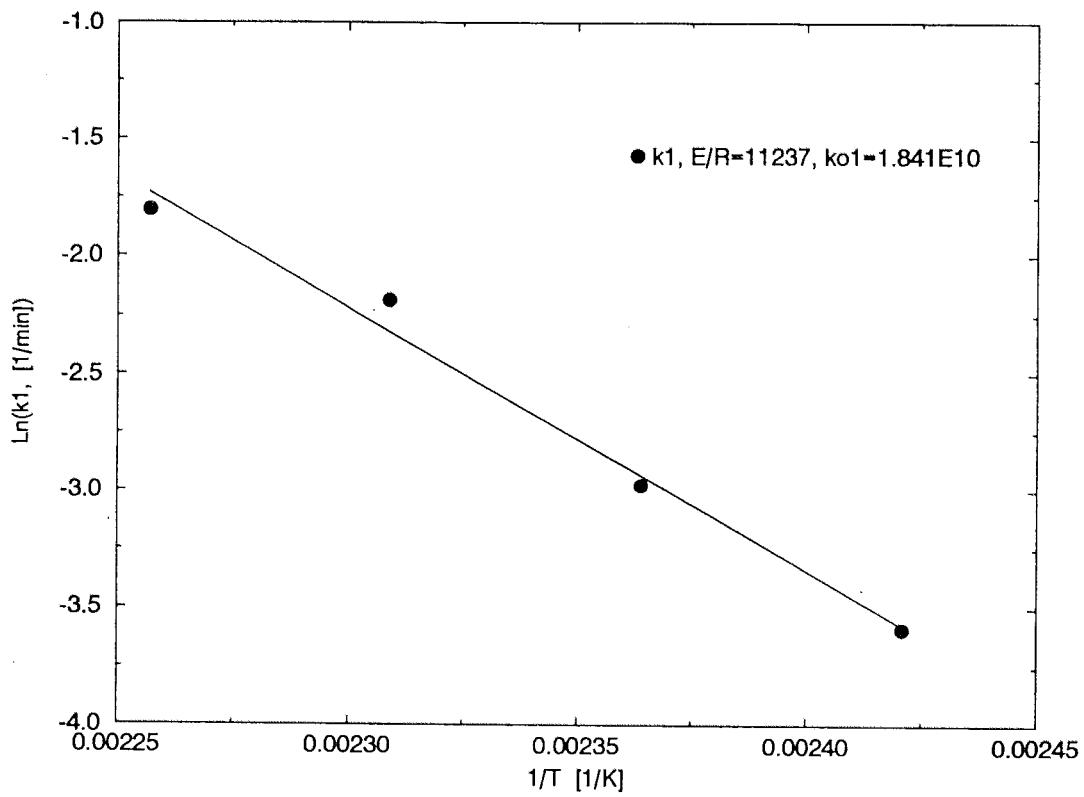


Figure 4. Arrhenius Equation for Hydrolysis of Hybrid Poplar Bark
(Solid:Liquid = 1:11.3)

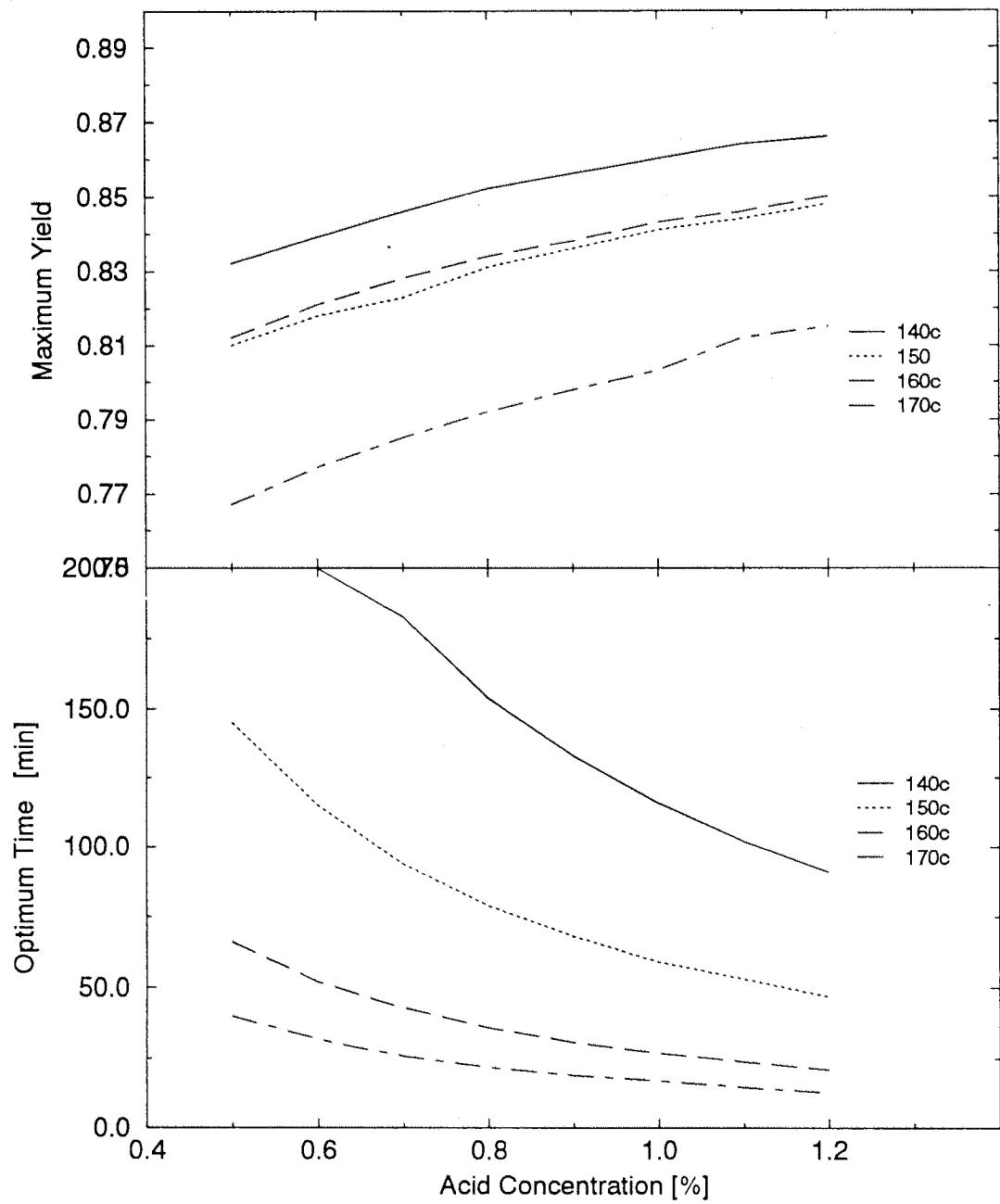


Figure 5. Modeling Optimum Condition in Hydrolysis of Hybrid Poplar Bark
(Solid:Liquid = 1:11.3)

TASK 2. Kinetics of Dilute Acid Pretreatment of Corn Cobs/Stover Mixture

The kinetic study for the pretreatment of Corn Cobs/Stover Mixture(CCSM) was carried out. The kinetics were modeled by a parallel hydrolysis of two fragments in hemicellulose followed by hydrolysis of oligomer, then decomposition of xylose. The kinetic parameters were determined from experimental data covering conditions of temperature of 120 - 150 °C, sulfuric acid concentration of 0.44 - 1.90% (corrected by the biomass buffer capacity), and liquid:solid ratio of 16.4:1.

EXPERIMENTAL METHODS

1. Sample Preparation

CCSM was supplied in the form of milled fine particles by NREL. The feedstock analysis was conducted following the NREL CAT Standard Procedures^[1,2,3,5, 6]. The results are shown in Table 5.

Table 5. Properties of Corn Cobs/Stover Mixture

Sugar:		[gram of sugar / gram of biomass (dry)]x100
Glucan:	39.2	
Xylan:	20.0	
Araban:	3.1	
Galactan:	1.2	
Mannan:	0.6	
Lignin:		[gram of lignin / gram of biomass (dry)]x100
Klason:	18.6	
Acid Soluble:	4.7	
Ash:	6.9	[gram of ash / gram of biomass (dry)]x100
Moisture:	8.0	[gram of water / gram of biomass (dry)]x100
Buffer Capacity ^a :	7.38	[mg of sulfuric acid / g. of biomass (dry)]x100

a: The buffer capacity of biomass was measured by titration method.

The buffer capacity in CCSM was determined to be 7.38 mg(sulfuric acid)/g biomass(dry). The acid concentration initially charged into the reactor were corrected accordingly, such that the four levels of acid concentrations of 0.49, 0.73, 1.22, and 1.95 wt% respectively were recalculated to be 0.44, 0.68, 1.17, 1.90 wt% respectively. The corrected values were applied in the kinetic study.

2. Batch Reactions

Reactions were carried out using pyrex glass tube reactors (11 mm i.d.). Glass tubes were packed with 0.4 g biomass and 6 ml acid solution, and sealed at both ends under natural gas - oxygen flame. To initial the reaction, the glass reactor ampules were placed into an oil bath (HAAKE FS2 model) in which the temperature was preadjusted to a temperature 50 °C higher than the desired reaction temperature. After 50 seconds, the ampules were transferred into another oil bath preset at the desired reaction temperature. The temperature measurement within the reactor has shown that the center section of the reactor reached the set point in 50 seconds. Temperature was measured by a thermocouple thermometer. The two oil bath procedure was done to minimize the preheating time. The time when the glass ampule was put into the second oil bath was set as the zero point of the reaction time. After being subjected to specified reaction times, the reactors were quenched in a cold water bath.

3. Analysis

Analyses for solid samples were performed by HPLC(Water Associate) using RI detector and a Bio-Rad's Aminex HPX-87P column. The column temperature was set at 85 °C and the DI water mobile phase flow rate was set at 0.6 ml/min. The liquid samples were analyzed by HPLC using RI detector and a Bio-Rad's Aminex HPX-87H column with column temperature at 65 °C and mobile phase of 0.005M sulfuric acid solution with flow rate at 0.6 ml/min. The Bio-Rad's Aminex HPX-87H column is not capable of separating xylose from mannose or galactose. However in our preliminary experimental runs, it is found that mannose in liquid samples less than 0.025 %, while galactose in liquid samples was found to be neglectable, based on the analytical results by Bio-Rad's HPX-87P column. Thus, it becomes suitable for liquid samples analysis by the Bio-Rad's Aminex HPX-87H column.

The kinetic data analysis was done on the basis of xylose equivalent. Where necessary the unreacted hemicellulose (xylan) was determined indirectly from material balance: unreacted xylan = initial xylan - xylose oligomer - xylose - furfural. Since the amount of furfural was much lower than other components, it was then neglected. In expressing xylan content, a weight gain factor for water addition in hydrolysis (168/150=1.14) was multiplied to simplify the stoichiometry of the reaction. For example, a sample containing 1 g xylan/100 mL was expressed as 1.12 g xylan as xylose/100 mL. The amount of soluble xylose oligomer in hydrolyzate from primary hydrolysis was measured as xylose by secondary hydrolysis with Cytolase CL enzyme.

A set of experiments was done to verify the above analytic method. The experiments of primary hydrolysis were done with CCSM at reaction conditions of 0.44% acid concentration, and 140 °C. The solid/liquid ratio maintained at 1:16.4 (0.4 gram wet biomass, 6 mL acid solution). The experiments of secondary hydrolysis were done to measure xylose-oligomer in the hydrolyzate by enzymatic hydrolysis at 50 °C, neutral pH and 24 hours, with enzyme loading of 10 IFPU/mL liquid (1:1 ratio mixing between diluted enzyme solution with 20 IFPU/mL, and neutralized primary hydrolyzate). The solid residues were washed with DI water to remove acid. The sugar analysis for solid residue were carried out according to the NREL CAT standard procedure^[2]. Table 6 shows the experimental results for the study of mass balance on xylose.

Table 6. Mass balance on xylose during hydrolysis of CCSM (Acid concentration: 0.44%, temperature: 140 °C)

Run #	Reaction time (min)	Liquid hydrolyzate				Solid residue	Total xylose obtained from liquid and solid residue	Percent of xylose obtained = total xylose obtained/ ini.xylan (%)
		Primary			Secondary			
		Xylose (g/100mL)	Ava. xylose (g/100mL)	Furfural (g/100mL)	Xylose (g/100mL)			
1a	10	0.238	0.256	-	0.732	0.476	0.652	1.384
1b		0.265		-				
1c		0.265		-				
2a	20	0.574	0.554	-	0.918	0.364	0.433	1.351
2b		0.533		-				
2c		0.555		-				
3a	30	0.704	0.702	-	0.978	0.276	0.358	1.336
3b		0.744		-				
3c		0.723		-				

Xylose oligomer as xylose = xylose in secondary hydrolyzate - xylose in primary hydrolyzate.

Initial xylan as xylose in each sample = 1.39 g/100mL.

The mass balances on xylose during reactions matched closely with the above method. The remaining xylan (measured) was slightly lower than the value calculated for those samples taken at late phase of the reaction. We found those samples contain more fine particles than that the ones taken at early phase. It is believed that small amount of the fine particles were lost during the washing process.

4. Kinetic Models

From our preliminary work, as shown in Figure 6, it was concluded that it would be appropriate to adopt the concept of biphasic hemicellulose such that:

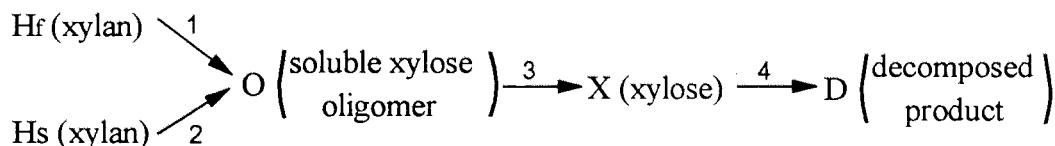


Figure 6. Acid Hydrolysis Pathway of CCSM Hemicellulose

For the proposed kinetic model, the variation of individual component can be theoretically determined by the following set of differential equations:

$$\frac{dH_f}{dt} = -k_1 A^{n_1} H_f \quad (4)$$

$$\frac{dH_s}{dt} = -k_2 A^{n_2} H_s \quad (5)$$

$$\frac{dO}{dt} = k_1 A^{n_1} H_f + k_2 A^{n_2} H_s - k_3 A^{n_3} O \quad (6)$$

$$\frac{dX}{dt} = k_3 A^{n_3} O - k_4 A X \quad (7)$$

with initial conditions:

- at $t = 0$, $H_f = F_f H_0$
- at $t = 0$, $H_s = (1 - F_f) H_0$
- at $t = 0$, $O = 0$
- at $t = 0$, $X = 0$

where:

- F_f = fast hydrolyzable fraction,
- H_0 = initial xylan content.

The analytical solutions for equations (6) and (7) were obtained as follows:

$$O = a_{11}(e^{-c_2 t} - e^{-c_5 t}) + a_{12}(e^{-c_4 t} - e^{-c_5 t}) \quad (8)$$

$$X = a_{21}(e^{-c_2 t} - e^{-c_6 t}) + a_{22}(e^{-c_4 t} - e^{-c_6 t}) + a_{23}(e^{-c_5 t} - e^{-c_6 t}) \quad (9)$$

where:

$$c_1 = k_1 A^{n_1} F_f H_0$$

$$c_2 = k_1 A^{n_1}$$

$$c_3 = k_2 A^{n_2} (1 - F_f) H_0$$

$$c_4 = k_2 A^n$$

$$c_5 = k_3 A^{n_3}$$

$$c_6 = k_4 A$$

$$a_{11} = \frac{c_1}{c_5 - c_2}$$

$$a_{12} = \frac{c_3}{c_5 - c_4}$$

$$a_{21} = \frac{c_1 c_5}{(c_5 - c_2)(c_6 - c_2)}$$

$$a_{22} = \frac{c_3 c_5}{(c_5 - c_4)(c_6 - c_4)}$$

$$a_{23} = -\frac{c_5}{c_6 - c_5} \left(\frac{c_1}{c_5 - c_2} + \frac{c_3}{c_5 - c_4} \right)$$

To determine the kinetic parameters in equations (8) and (9) simultaneously, a SAS NLIN Program was used to regress the following objective function:

$$Y = O^2 + X^2 \quad (10)$$

EXPERIMENTAL RESULTS AND DISCUSSION

1. Selection of Reaction Conditions

It appears that a high liquid/solid ratio is required to ensure uniform wetting condition of

CCSM. We have applied the L/S ratio of 16.4:1 in our glass ampule reactor experiments. This value is much higher than those applied in pretreatment of Switchgrass or Hybrid Poplar Bark. It is not suggested that the high L/S ratio has to be used in the actual processing of biomass. The high liquid amount in our kinetic experiments was applied to eliminate any possibility of non-uniform wetting, and acid gradient in the biomass. We did, however, notice that the swelling of ground CCSM is indeed higher than that of Switchgrass or Hybrid Poplar Bark.

In order to verify the kinetics of hemicellulose hydrolysis, batch experiments were conducted according to the procedure described previously. After reviewing the results of preliminary runs, the experimental conditions were set to cover 0.49 - 1.95 wt% (without correction for biomass buffer capacity) sulfuric acid and 120 - 150 °C reaction temperature.

To measure the soluble xylose oligomer content in hydrolyzate, a secondary hydrolysis was conducted by using cellulase enzyme (Cytolase, Lot No. 17-92262-09, supplied by Environmental Biotech.), at 50 °C, neutral pH, and 24 hours. The secondary hydrolysis can be fulfilled at this condition without any xylose decomposition. The concentrations of both xylose and glucose were seen to increase, a proof that the hydrolyzate contain oligomer as well as monomers. The concentration of oligomer content, therefore, can be calculated by the difference of monomer concentrations between primary and secondary hydrolyzate.

2. Determination of Model Parameters

The results of xylan hydrolysis in CCSM are shown in Figure 7. The residual xylan concentration were plotted against reaction time for various conditions. The sharp breakage in the semi-log plot indeed confirmed that the xylan in CCSM is composed of two different fragments.

Variation of oligomer content throughout the acid pretreatment reaction is shown in Figure 8. As was the case with Switchgrass, oligomer formation at the early phase of the reaction is quite high. It is then gradually converted to monomer (xylose) at the later phase of the reaction. Based on the reaction conditions, a higher temperature and higher acid concentration resulted less oligomer.

Thus, equations (8) and (9) are suitable to represent the relations of changing of xylose and soluble xylose oligomer with time. Equation (10) can be used to determine the kinetic model parameters. The fast hydrolyzable fragment was determined statistically by non-linear regression analysis using a SAS NLIN program (see Appendix 4). In the procedure, the experimental data at 120, 130, 140 and 150 °C were used to fit equation (10). Having the xylose decomposition data $k_4 A$ value for various reaction conditions from Kim and Lee^[4], with randomly giving F_f , n_1 , n_2 and n_3 by try and error, the remaining 12 parameters (four each for k_1 , k_2 and k_3 at four different temperature level) were determined employing data from 16 experimental runs. The F_f value of 0.6-0.8, n_1 , n_2 , and n_3 values of 0-3.0 were given to fit the model by comparing the sum of squares. During the regression, the best fitting F_f value was found to be 0.65. Similarly, the best

fitting values for n_1 , n_2 and n_3 were found to be 1.0, 1.0 and 1.2 respectively.

The resulting kinetic parameters are shown in Table 7. The statistical analysis has shown the upper limit of the standard deviations of all the kinetic parameters was less than 26 % (see Appendix 5 "Modelling results of CCSM Hydrolysis").

By applying Arrhenius equation for k_1 , k_2 and k_3 , it is shown in Figure 9 that the resulting kinetic parameters were in good agreement with Arrhenius equation. Table 8 is the activation energy for reaction 1, 2 and 3. Of particular significance in this result is that the maximum yield ([xylose+soluble xylose oligomer]/initial xylan as xylose) from the model was found to be independent of acid concentration, as shown in Figure 10. The optimum temperature is about 130-140 °C. However, the reaction time decreases considerably as the concentration increases. The reaction time reaching the maximum yield is much shorter at 140 °C than the one at 130 °C. We have also tested the model for the temperature of 125 and 135 °C. In both cases, we obtained about the same value of yield as that at 140 °C. Obviously, longer time is needed at 125 or 135 °C than at 140 °C. By considering the factor of the reaction time, we would like to conclude that the optimum operating temperature is 140 °C.

Four additional runs of hydrolysis were made to verify the optimum reaction condition given by the reaction model. The experimental results were listed in Table 9. The temperature of 140 oC was selected because it is the optimum reaction temperature. As shown in Figure 10, there is an excellent agreement between the experimental data and the prediction by the reaction model. As stated before, the optimum yield is independent of acid concentration. However, the optimum time at which attains optimum yield is shorter under high acid concentration. We have also found that small amount of furfural was formed when reaction approached the optimum point. To decrease the formation of furfural, it is suggested that the actual reaction time be reduced somewhat from the theoretical optimum time. For this purpose, we included Figure 11 which shows the relation between yield and reaction time. It is clearly seen that the reaction time can be decreases as much as 20% of optimum time without appreciable loss of yield.

The comparison between the predicted reaction progress calculated from the kinetic model and the associated parameters, and the actual experimental data are shown in Appendix 6. The model prediction is seen to be in good agreement with the experimental data, thus confirming that the proposed model and the associated kinetic parameters are valid for hydrolysis of CCSM hemicellulose.

SUMMARY

1. The ground CCSM has a high swelling property.
2. The hemicellulose in CCSM is of biphasic in dilute-acid hydrolysis.
3. The overall kinetics is such that high temperature and high acid concentration induces less oligomer formation.
4. Maximum yield of xylose+soluble xylose oligomer in the hydrolysis is relatively independent of acid concentration over the range of 0.44 - 1.90% (corrected by the biomass buffer capacity).
5. The activation energies for hydrolysis is slightly lower than that of decomposition. The theoretical yield of xylose+xylose oligomer as function of temperature is rather complicated; achieving 90% yield at 130-140 °C and 88% yield at 120 and 150 °C.
6. The optimum operating temperature over the aforementioned acid concentration range is about 140 °C considering both the yield and the reaction time.
7. The biphasic kinetic model with the provision kinetic parameters has shown a reliable prediction of the time course variation of xylose.
8. The model was somewhat less reliable in predicting soluble xylose oligomer content in the early phase of the reaction, showing maximum asymptotic standard error of 26 %.
9. The proposed model and the associated kinetic parameters are valid for hydrolysis of CCSM hemicellulose.

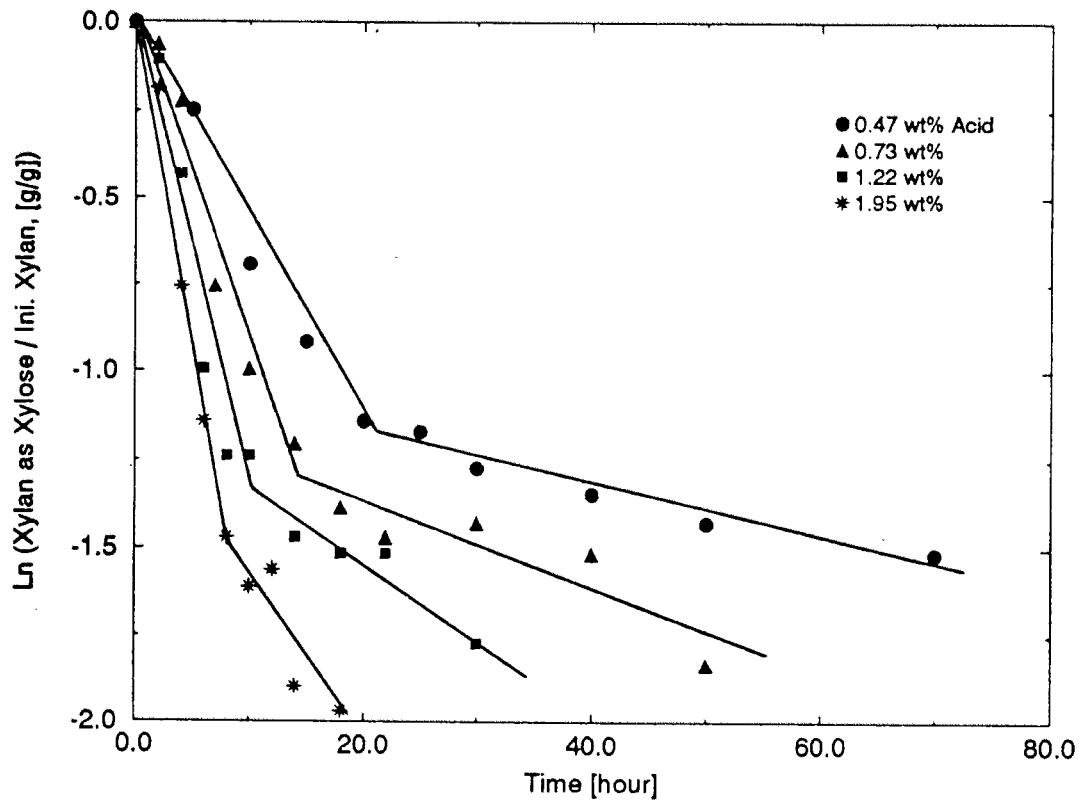


Figure 7. Decay of Xylan Content in CCSM Hemicellulose during Hydrolysis
(Temperature= 140 °C, Solid:Liquid = 1:16.4)

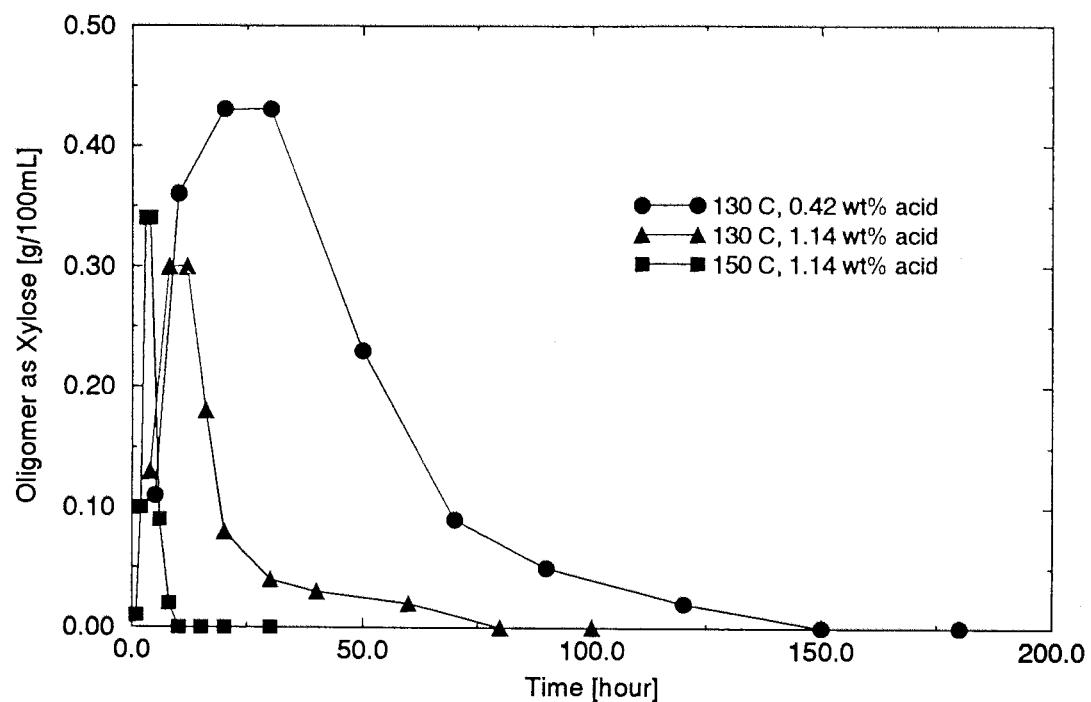


Figure 8. Profile of Xylose Oligomer Formed during Hydrolysis of CCSM
(Solid:Liquid = 1:16.4)

Table 7. Kinetic Parameters from Modeling^a

Temperature (°C)	k_1 [min ⁻¹ (%w/w) ^{-1.0}]	k_2 [min ⁻¹ (%w/w) ^{-1.0}]	k_3 [min ⁻¹ (%w/w) ^{-1.2}]	k_4^b [min ⁻¹ (%w/w)]
120	0.0660	0.00453	0.0453	0.000226
130	0.1546	0.01424	0.1482	0.000550
140	0.2581	0.03169	0.3019	0.001280
150	0.4417	0.05602	0.5692	0.002917

a: $F_f=0.65$; n_1 , n_2 and $n_3=1.0$, 1.0 and 1.2 respectively.

b: After Kim and Lee⁽⁴⁾

Table 8. Activation Energy for Each Reactions.

k_i	k_{oi} [min ⁻¹ (%w/w) ⁻ⁿⁱ]	n_i	E_i [kcal/g mol]
1	1.998×10^{10}	1.0	20.6
2	1.237×10^{13}	1.0	27.7
3	1.046×10^{14}	1.2	27.5
4 ^a	8.990×10^{11}	1.0	28.2

a: After Kim and Lee⁽⁴⁾

Table 9. Verification of the optimum yield

Run #	Acid Concentration (%)	Optimum Reaction Time (min)	Xylose Concentration (g/100mL)	Furfural Concentration (g/100mL)	Yield (%)
y1	1.90	38	1.240	0.034	89.2
y1a	1.90	38	1.260	0.033	90.6
y2	1.17	61	1.232	0.027	88.6
y3	0.68	105	1.222	0.026	88.0

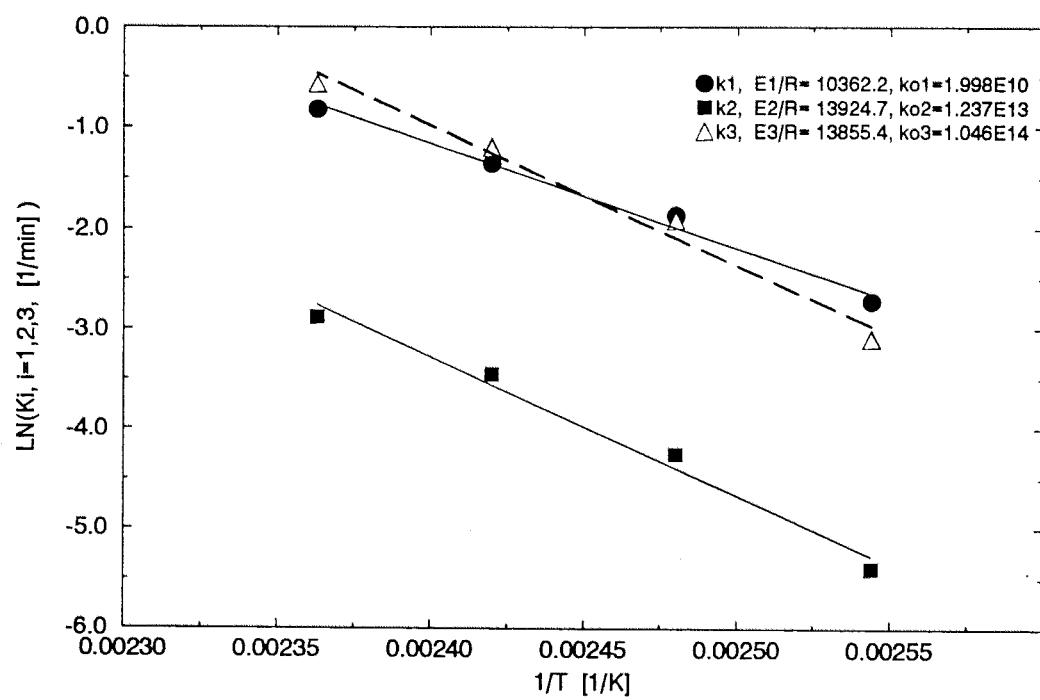


Figure 9. Arrhenius Equation for Hydrolysis of CCSM
 (Solid:Liquid = 1:16.4)

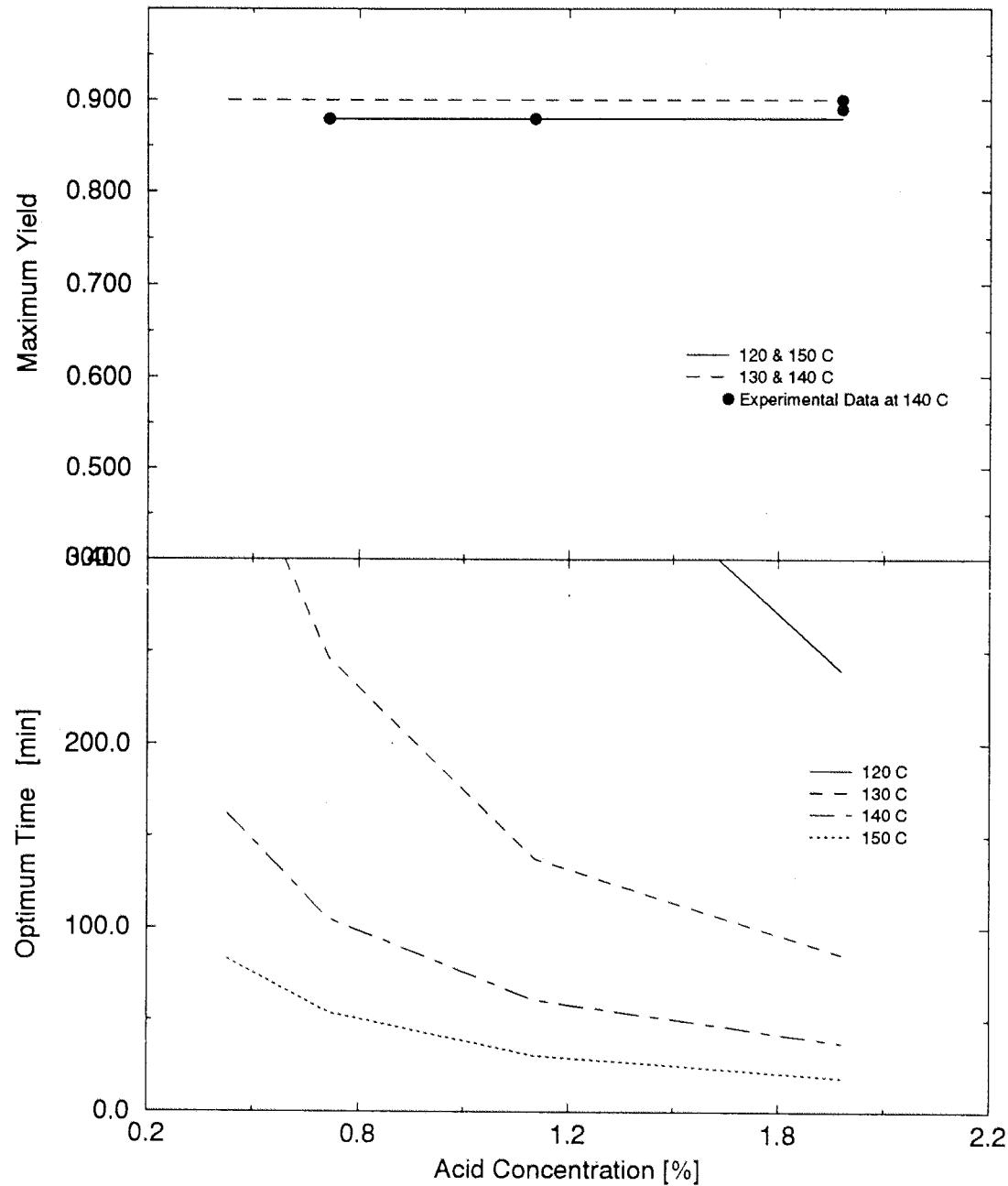


Figure 10. Modeling Optimum Condition in Hydrolysis of CCSM
(Solid:Liquid = 1:16.4)

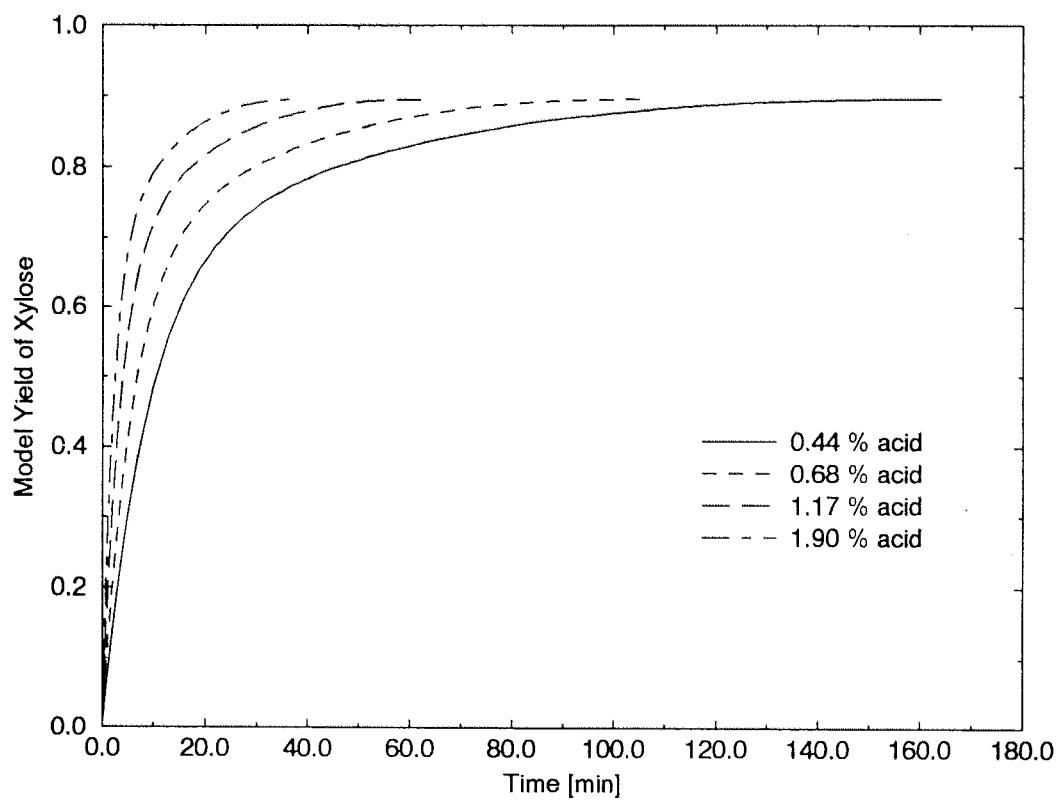


Figure 11. Model Yield Versus Reaction Time
(Temperature = 140 °C, Solid:Liquid = 1:16.4)

TASK 3. Determination of Thermal Diffusivities for Hybrid Poplar Bark, Switchgrass, and Corn Cobs/Stover Mixture.

The experimental work concerning the thermal diffusivity determination for biomass feedstocks, such as Hybrid Poplar Bark (HPB), Switchgrass (SG), and Corn Cobs/Stover Mixture (CCSM), were carried out during the past year. The experimental method is based upon the dynamic response against the step-change input of external temperature. The experimental work thus involved measurement of the temperature change in the center-point of the sample cell containing the biomass feedstocks in the form of a thick slurry. The thermal diffusivities of HPB, SG, and CCSM were experimentally determined by SAS nonlinear programs.

EXPERIMENTAL METHODS

1. Sample Cell Preparation

The biomass feedstocks, HPB, SG, and CCSM, were supplied in the form of fine particles by NREL. The objective here was to measure the thermal diffusivities of wet slurry in a packed state as it exists in the percolation reactor. A special type of sample holder was designed and constructed for this purpose (Figure 12). It consists of one non-metal cylinder with a thick wall (round surface), and two thin aluminum sheets (flat surface covering top and bottom surfaces). The ratio of the distance in the direction in which thermal diffusivities were determined to the distance in the other direction, h/D , is at least 1 to 5. The non-heat-transfer surface (cylinder wall) was covered by a silicone insulator/sealant. This was done to minimize the heat transfer through the radial direction, thus forcing a uni-directional heat flow. The cell size in our experiments is $h=2.6$ cm, $D=13$ cm. The cells containing biomass feedstocks were impregnated in water for at least 24 hours before being used in experiments. The moisture content of the slurry biomass samples are listed in Table 10.

Table 10. Moisture Contents of the Slurry Samples in Cells

HPB (wt %)	SG (wt %)	CCSM (wt %)
80.0	85.2	91.1

2. Experimental Setup

The overall experimental setup is shown in Figure 13. The surrounding temperature was set by a water bath. A thermocouple measures the temperature profile at the center point of the sample cells. The input signal from thermocouple was processed through a signal amplifier, an A to D convertor, and finally logged into a personal computer for recording temperature.

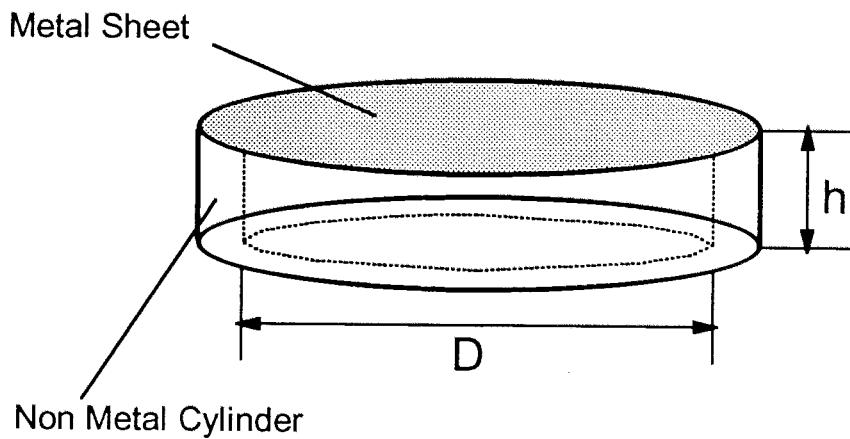


Figure 12. Sample Holder for Packed Wet Biomass Slurry
Used for Measurement of Thermal Diffusivity

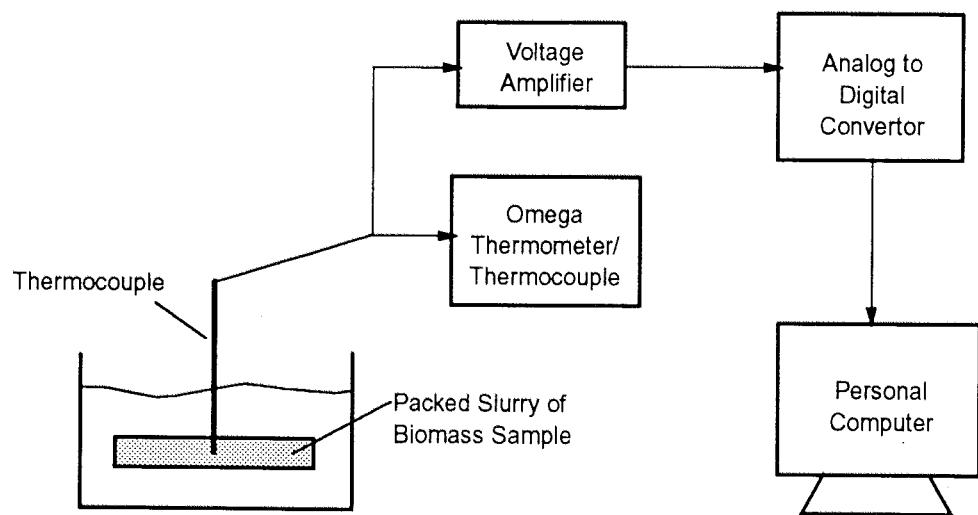


Figure 13. Schematics of the Experimental Setup

HEAT TRANSFER THEORY

A heat balance within a differential segment of a biomass feedstock in a sample cell results in an unsteady state conduction equation,

$$\frac{\delta T}{\delta t} = \alpha \frac{\delta^2 T}{\delta x^2} \quad (11)$$

with the boundary conditions of

$$x = 0, \frac{\delta T}{\delta t} = 0 \quad (12)$$

$$x = L, \frac{\delta T}{\delta t} = -h(T - T_s)/k \quad (13)$$

and the initial condition

$$t = 0, T = T_0 \quad (14)$$

where

T = Temperature

t = Time

x = Thickness measured from the center

α = Thermal diffusivity

T_s = Surrounding water temperature

T₀ = Initial temperature

k = Thermal conductivity

h = Heat transfer coefficient

L = Half the thickness of the slab

Using the following transformation, equations (11) through (14) become dimensionless

$$z = x/L$$

$$\tau = \alpha t / L^2$$

$$\theta = (T - T_s) / (T_0 - T_s)$$

and equation (1) through (4) become

$$\frac{\delta \theta}{\delta \tau} = \frac{\delta^2 \theta}{\delta z^2} \quad (15)$$

$$z = 0, \frac{\delta \theta}{\delta z} = 0 \quad (16)$$

$$z = 1, \frac{\delta \theta}{\delta z} + Nu \cdot \theta = 0 \quad (17)$$

$$\tau = 0, \theta = 1 \quad (18)$$

where

$$Nu = hL/k$$

The Nu values were large enough to assume the boundary condition of $T = Ts$ at $x = L$, the general analytical solution to equation (15), after application of corresponding boundary conditions and initial condition, may be written as

$$\theta = 2 \sum \frac{(-1)^n}{\lambda_n} \exp(-\lambda_n^2 \tau) \cos(\lambda_n z) \quad (19)$$

where

$$\lambda_n = (2n+1)\pi/2$$

This solution is graphically presented in Figure 14 showing the variation of θ as a function of dimensionless distance (z) and time (τ).

DETERMINATION OF THERMAL DIFFUSIVITIES

The experimental data (time course of center-point temperature) for the biomass feedstocks were incorporated into Equation (19), and put through a SAS Non-Linear Regression Program. The regression then yielded the objective parameter values, the thermal diffusivities of the biomass samples, the thick biomass slurry in this case. During the regression, the first eight terms of the infinite series in Equation (19) were used in the calculations. More terms had been tried. No significant improvement, however, was observed in the sum of square of errors.

By employing the experimental data from different temperature, the regression resulted the thermal diffusivities of the biomass feedstocks at different temperature. As shown in Figure 15, the thermal diffusivities of HPB, SG, and CCSM all increase with the system temperature. The thermal diffusivities of these biomass samples are more sensitive to temperature than pure water. The thermal diffusivities of CCSM slurry is lower than that of HPB slurry, but higher than that of SG slurry. By linearizing the thermal diffusivity data obtained at various temperature, three working equations were resulted in Table 11 for the thermal diffusivities of the biomass feedstocks as functions of temperature.

Table 11. Thermal Diffusivities of HPB, SG, and CCSM

Sample of Biomass Slurry	Thermal Diffusivity, α [m ² /s]
Hybrid Poplar Bark	$(0.6918 + 0.01787 * T[\text{°C}]) * 10^{-7}$
Switchgrass	$(0.4771 + 0.01331 * T[\text{°C}]) * 10^{-7}$
Corn Cobs/Stover Mixture	$(0.6024 + 0.01301 * T[\text{°C}]) * 10^{-7}$

The temperature range applicable for those equation in Table 11 is 30.4 - 86.0 °C. The regression programs with raw data are listed in Appendix 7. The statistical output of the regression work for HPB, SG, and CCSM are shown in Appendix 8, from which we can see that the upper limits of the standard deviations of the diffusivities are less than 3.8 % for HPB, 1.9 % for SG, and 0.81 % for CCSM respectively. The comparisons between the predicted temperature profiles calculated from Equation (19) with the thermal diffusivities from Table 11, and the actual experimental data are shown in Appendix 9. The predictions are seen to be in good agreement with the experimental data.

SUMMARY

1. The thermal diffusion apparatus described in Figure 12 and 13 are functional and effective in the determination of the thermal diffusivity of biomass in the form of fine particles.
2. The thermal diffusivities of HPB, SG, and CCSM are rather sensitive to the system temperature.
3. The thermal diffusivities of HPB with 80 % moisture content, SG with 85.2 % moisture content, and CCSM with 91.1 moisture were determined to be $(0.6918+0.01787*T[^{\circ}C])*10^{-7}$, $(0.4771+0.01331*T[^{\circ}C])*10^{-7}$, and $(0.6024+0.01301*T[^{\circ}C])*10^{-7}$ respectively within the temperature range of 30.4 - 86.0 °C.
4. The predicted temperature profiles calculated from Equation (19) with associated thermal diffusivities are in good agreement with the experimental data.
5. The thermal diffusivities of CCSM slurry is lower than that of HPB slurry, but higher than that of SG slurry.

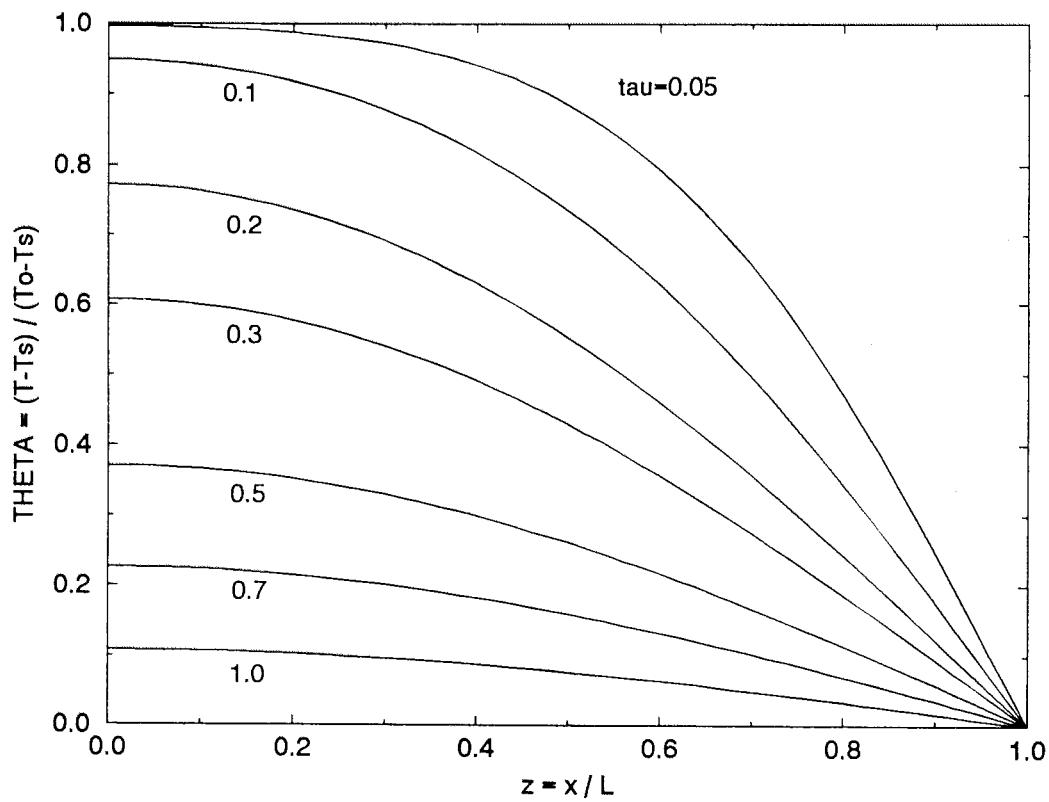
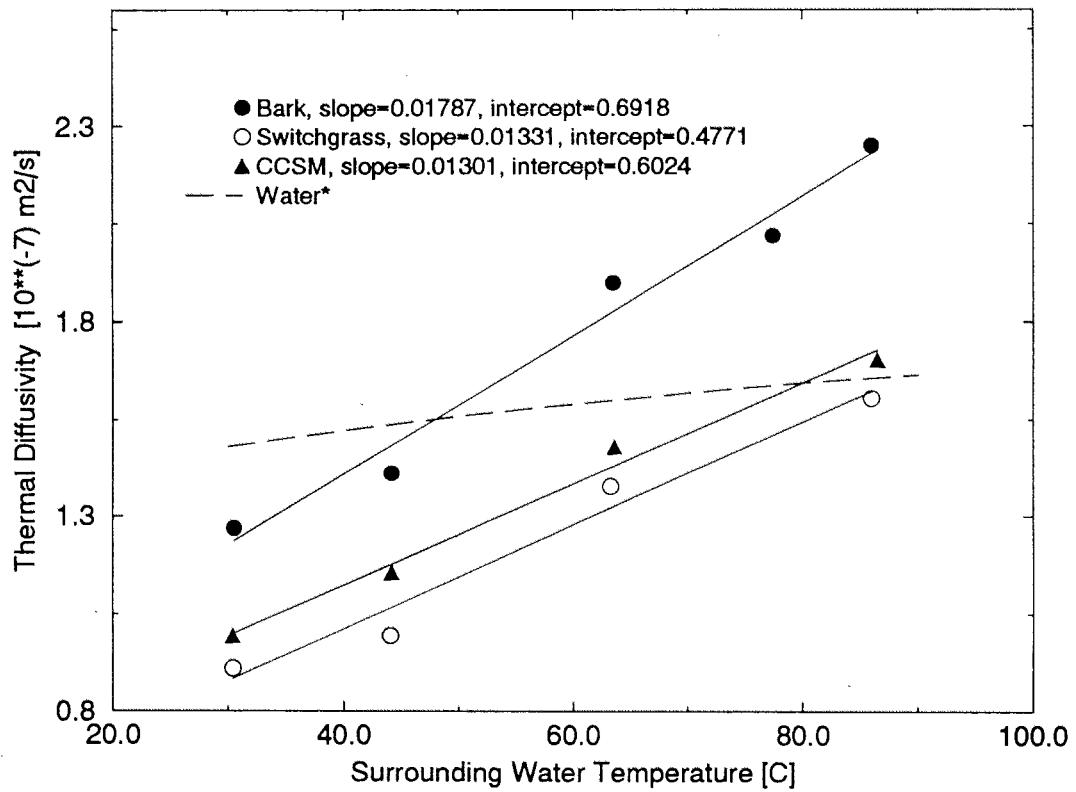


Figure 14. Temperature Profiles for Unsteady-State Heat Conduction in a Sample Cell



(*: Data from Hanfbook of Chemistry and Physics, CRC press, 58th Edition, 1977-1988)

Figure 15. Temperature Effect on Thermal Diffusivities

REFERENCES

1. NREL Chemical Analysis & Testing Standard Procedure No. 001, "Determination of Total Solid/Moisture in Biomass", Aug. 1992.
2. NREL Chemical Analysis & Testing Standard Procedure No. 002, "Two Stage Sulfuric Acid Hydrolysis for Determination of Carbohydrates", Aug. 1992.
3. NREL Chemical Analysis & Testing Standard Procedure No. 003, "Determination of Klason Lignin in Biomass", Aug. 1992.
4. Kim and Lee, Biotechnol. and Bioeng., Symp. No.17, 21-84, 1986
5. NREL Chemical Analysis & Testing Standard Procedure No. 004, "Determination of Acid Soluble Lignin in Biomass", Aug. 1992.
6. NREL Laboratory Analytical Procedure LAP-005, "Standard Method for Ash in Biomass", April 1994.

Appendix 1.

SAS Program with Raw Data for Determination of

Model Parameters in Hydrolysis of Hybrid Poplar Bark

```

title 'Modelling Result of Hybrid Poplar Bark Hydrolysis at 140c';

data bark;
  n=1.4;
  kk3=0.001301;
  h0=1.49;
  input a t x;
cards;
0.42 15 0.09
0.42 30 0.29
0.42 45 0.39
0.42 60 0.53
0.42 75 0.61
0.42 90 0.64
0.42 130 0.77
0.42 150 0.86
0.42 180 0.99
0.66 10 0.09
0.66 20 0.32
0.66 30 0.52
0.66 40 0.67
0.66 50 0.79
0.66 60 0.88
0.66 100 1.15
0.66 151 1.27
0.66 5 0.07
0.66 10 0.15
0.66 15 0.24
0.66 20 0.35
0.66 25 0.48
0.66 30 0.61
0.66 40 0.77
0.66 55 0.89
0.66 60 0.95
0.66 80 0.98
1.14 5 0.19
1.14 10 0.43
1.14 15 0.64
1.14 20 0.77
1.14 30 1.01
1.14 40 1.22
1.14 50 1.23
1.14 80 1.36
1.87 4 0.38
1.87 8 0.70
1.87 16 1.02
1.87 20 1.11
1.87 25 1.15
1.87 30 1.19
1.87 40 1.20
1.87 70 1.31
run;

```

```
proc nlin data=bark;  
  
parm kk1=0.0001;  
      k1=kk1*a**n;  
      k3=kk3*a;  
  
model x=h0*k1/(k3-k1)*(exp(-k1*t)-exp(-k3*t));  
  
der.kk1=(h0/(k3-k1)*(exp(-k1*t)-exp(-k3*t))  
        +h0*k1/(k3-k1)**2*(exp(-k1*t)-exp(-k3*t))  
        -h0*k1/(k3-k1)*t*exp(-k1*t))*a**n;  
run;
```

```
title 'Modelling Result of Hybrid Poplar Bark Hydrolysis at 150C'; -- DATA SET ONLY
```

```
data bark;
  n=1.4;
  kk3=0.002917;
  h0=1.49;
  input a t x;
cards;
0.42 10 0.12
0.42 20 0.21
0.42 30 0.33
0.42 40 0.61
0.42 50 0.72
0.42 60 0.81
0.42 100 1.10
0.42 150 1.24
0.66 4 0.08
0.66 8 0.19
0.66 12.5 0.37
0.66 16 0.45
0.66 20 0.60
0.66 30 0.84
0.66 40 0.98
0.66 55 1.05
0.66 90 1.10
1.14 2 0.19
1.14 5 0.31
1.14 8 0.67
1.14 12 0.89
1.14 16 1.08
1.14 20 1.17
1.14 25 1.25
1.14 30 1.29
1.14 40 1.34
1.14 60 1.35
1.87 2 0.17
1.87 5 0.71
1.87 8 0.92
1.87 11 1.05
1.87 20 1.20
1.87 25 1.25
1.87 30 1.30
1.87 40 1.27
run;
```

```

title 'Modelling Result of Hybrid Poplar Bark Hydrolysis at 160c'; -- DATA SET ONLY

data bark;
  n=1.4;
  kk3=0.006302;
  h0=1.49;
  input a t x;
cards;
0.42 10 0.33
0.42 20 0.74
0.42 30 0.92
0.42 40 1.13
0.42 50 1.18
0.42 60 1.22
0.42 80 1.15
0.42 100 1.17
0.42 120 1.09
0.42 140 1.12
0.66 3 0.16
0.66 6 0.46
0.66 9 0.50
0.66 12 0.80
0.66 15 1.09
0.66 20 1.22
0.66 30 1.21
0.66 40 1.23
0.66 60 1.26
0.66 80 1.11
1.14 2 0.12
1.14 5 0.99
1.14 8 1.08
1.14 14 1.21
1.14 17 1.25
1.14 20 1.30
1.14 25 1.26
1.14 35 1.28
1.14 45 1.21
1.87 1 0.09
1.87 2 0.27
1.87 3 0.76
1.87 4 0.86
1.87 6 1.11
1.87 8 1.14
1.87 10 1.13
1.87 13 1.21
1.87 16 1.16
1.87 20 1.17
run;

```

```

title 'Modelling Result of Hybrid Poplar Bark Hydrolysis at 170c'; -- DATA SET ONLY

data bark;
  n=1.4;
  kk3=0.013150;
  h0=1.49;
  input a t x;
cards;
0.42 4 0.10
0.42 8.33 0.40
0.42 12 0.65
0.42 16 0.75
0.42 20 0.90
0.42 25 1.01
0.42 40 1.15
0.42 55 1.11
0.42 70 1.07
0.66 2.25 0.12
0.66 4 0.32
0.66 6 0.55
0.66 8 0.75
0.66 10 1.03
0.66 12 1.10
0.66 16 1.24
0.66 20 1.21
0.66 30 1.21
0.66 40 1.17
1.14 1 0.16
1.14 2 0.33
1.14 3 0.59
1.14 4 0.96
1.14 6 1.15
1.14 8 1.25
1.14 13 1.29
1.14 16 1.26
1.14 20 1.20
1.87 1 0.18
1.87 2 0.49
1.87 3 0.90
1.87 4 1.15
1.87 5 1.18
1.87 6 1.22
1.87 7 1.24
1.87 9 1.24
1.87 12 1.19
1.87 15 1.15
run;

```

Appendix 2.

Modeling Results of Hybrid Poplar Bark Hydrolysis

Modelling Result of Hybrid Poplar Bark Hydrolysis at 140c 13
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable X Method: Gauss-Newton

Iter	KK1	Sum of Squares
0	0.000100	28.312660
1	0.011467	5.115730
2	0.022741	0.513940
3	0.027301	0.233962
4	0.027690	0.232495
5	0.027689	0.232495
6	0.027689	0.232495

NOTE: Convergence criterion met.

Modelling Result of Hybrid Poplar Bark Hydrolysis at 140c 14
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable X

Source	DF	Sum of Squares	Mean Square
Regression	1	28.504704598	28.504704598
Residual	42	0.232495402	0.005535605
Uncorrected Total	43	28.737200000	
(Corrected Total)	42	6.011906977	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
KK1	0.0276887471	0.00076182824	0.02615132163 0.02922617253

Modelling Result of Hybrid Poplar Bark Hydrolysis at 140c 15
20:47 Saturday, February 12, 1994

Asymptotic Correlation Matrix

Corr	KK1
KK1	1

Modelling Result of Hybrid Poplar Bark Hydrolysis at 150c 16
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable X Method: Gauss-Newton

Iter	KK1	Sum of Squares
0	0.000100	28.450105
1	0.017768	5.817372
2	0.037889	0.799353
3	0.049633	0.317981
4	0.051014	0.314101
5	0.050957	0.314094
6	0.050960	0.314094
7	0.050960	0.314094

NOTE: Convergence criterion met.

Modelling Result of Hybrid Poplar Bark Hydrolysis at 150c 17
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable X

Source	DF	Sum of Squares	Mean Square
Regression	1	28.408405747	28.408405747
Residual	34	0.314094253	0.009238066
Uncorrected Total	35	28.722500000	
(Corrected Total)	34	5.985240000	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
-----------	----------	-----------------------	-------------------------------------

KK1	0.0509600297	0.00213084146	0.04662966571	0.05529039371
-----	--------------	---------------	---------------	---------------

Modelling Result of Hybrid Poplar Bark Hydrolysis at 150c 18
20:47 Saturday, February 12, 1994

Asymptotic Correlation Matrix

Corr	KK1
KK1	1

Modelling Result of Hybrid Poplar Bark Hydrolysis at 160c 19
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable X Method: Gauss-Newton

Iter	KK1	Sum of Squares
0	0.000100	41.117839
1	0.029203	9.786994
2	0.065496	2.062975
3	0.099078	0.641041
4	0.111642	0.563176
5	0.112309	0.563011
6	0.112290	0.563011
7	0.112291	0.563011

NOTE: Convergence criterion met.

Modelling Result of Hybrid Poplar Bark Hydrolysis at 160c 20
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable X

Source	DF	Sum of Squares	Mean Square
Regression	1	40.784888768	40.784888768
Residual	38	0.563011232	0.014816085
Uncorrected Total	39	41.347900000	
(Corrected Total)	38	4.923897436	

Parameter Estimate Asymptotic Asymptotic 95 %
 Std. Error Confidence Interval
 Lower Upper

KK1 0.1122908091 0.00627498424 0.09958783265 0.12499378564

Modelling Result of Hybrid Poplar Bark Hydrolysis at 160c 21
20:47 Saturday, February 12, 1994

Asymptotic Correlation Matrix

Corr	KK1
KK1	1

Modelling Result of Hybrid Poplar Bark Hydrolysis at 170c 22
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable X Method: Gauss-Newton

Iter	KK1	Sum of Squares
0	0.000100	35.735157
1	0.050181	8.059772
2	0.112506	1.347671
3	0.158030	0.523367
4	0.165038	0.514120
5	0.164471	0.514066
6	0.164532	0.514065
7	0.164526	0.514065
8	0.164526	0.514065

NOTE: Convergence criterion met.

Modelling Result of Hybrid Poplar Bark Hydrolysis at 170c 23
20:47 Saturday, February 12, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable X

Source	DF	Sum of Squares	Mean Square
Regression	1	35.338435028	35.338435028
Residual	37	0.514064972	0.013893648
Uncorrected Total	38	35.852500000	
(Corrected Total)	37	5.485107895	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
KK1	0.1645263744	0.00852622644	0.14725069175 0.18180205700

Modelling Result of Hybrid Poplar Bark Hydrolysis at 170c 24
20:47 Saturday, February 12, 1994

Asymptotic Correlation Matrix

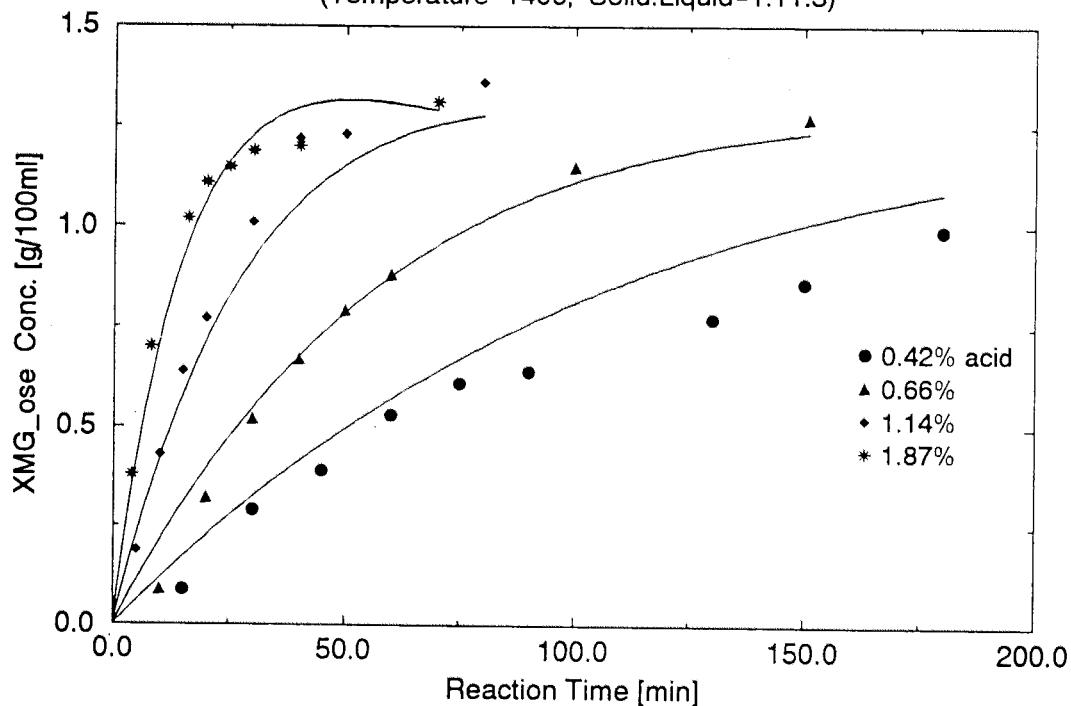
Corr	KK1
KK1	1

Appendix 3.

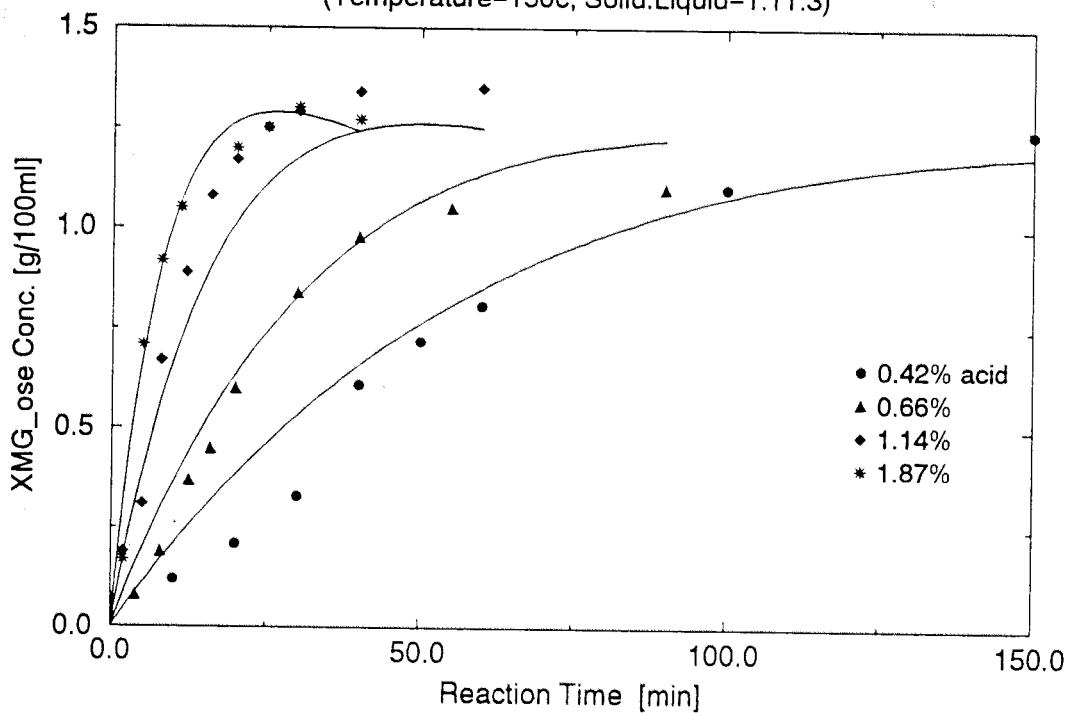
Comparison Between Experimental and Model Values for

Reaction Progression in Hydrolysis of Hybrid Poplar Bark

Reaction Progression in Hybrid Poplar Bark Hydrolysis
(Temperature=140c, Solid:Liquid=1:11.3)

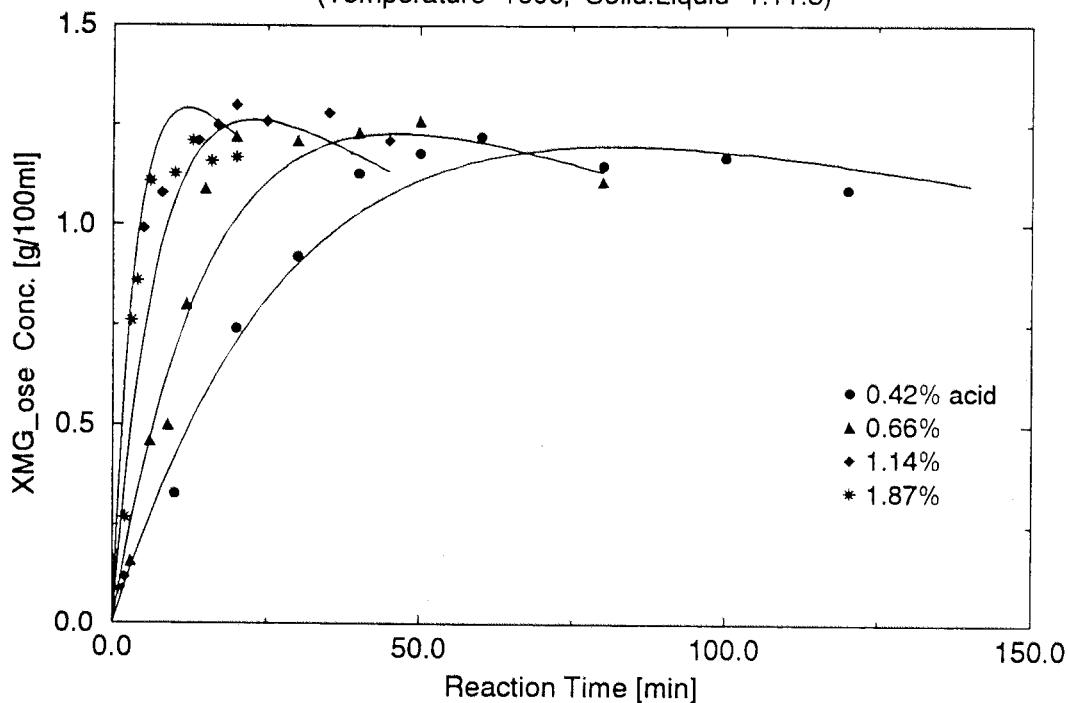


(Temperature=150c, Solid:Liquid=1:11.3)

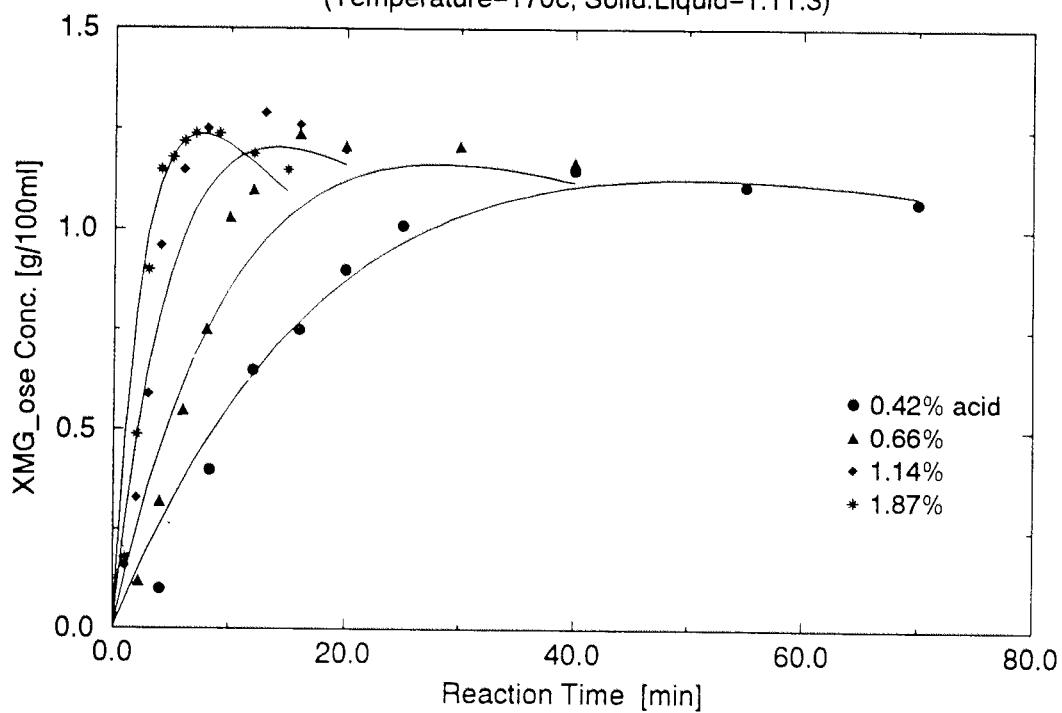


(--: Best Fit for Individual Run)

Reaction Progression in Hybrid Poplar Bark Hydrolysis
(Temperature=160c, Solid:Liquid=1:11.3)



(Temperature=170c, Solid:Liquid=1:11.3)



(--: Best Fit for Individual Run)

Appendix 4.

SAS Program with Raw Data for Determination of

Model Parameters in Hydrolysis of Corn Cobs/Stover Mixture

```

title 'Modelling Result of CCSM Hydrolysis at 120c';
data oligoaa;
  kk4=0.00023;

  ff1=0.65;
  ff2=1-ff1;

  H0=1.39;
  f1=ff1*H0;
  f2=ff2*H0;
  input a t x o;
  cards;
0.44 15 .10 .20
0.44 30 .18 .41
0.44 60 .33 .40
0.44 81 .45 .36
0.44 100 .50 .31
0.44 120 .65 .21
0.44 140 .73 .15

0.68 10 .09 .24
0.68 20 .16 .38
0.68 30 .33 .40
0.68 40 .42 .37
0.68 50 .51 .28
0.68 60 .60 .25
0.68 80 .75 .16
0.68 100 .92 .03
0.68 120 .92 .01
0.68 140 .98 .0

1.17 5 .06 .08
1.17 10 .14 .45
1.17 15 .26 .47
1.17 20 .44 .31
1.17 30 .63 .26
1.17 40 .81 .14
1.17 60 .94 .12
1.17 80 1.01 .02
1.17 100 1.04 .01
1.17 120 1.06 .0

1.90 5 .06 .24
1.90 10 .27 .37
1.90 15 .56 .27
1.90 20 .67 .19
1.90 25 .81 .12
1.90 40 .96 .03
1.90 50 .99 .02
1.90 60 1.07 .0
1.90 70 1.08 .0

run;

```

```

data oli;
  set oligoaa;
  kk4=kk4;

  a1=a**1.0;
  a2=a**1.0;
  a3=a**1.2;
  a4=a;

  t=t;
  y=x**2+o**2;

  f1=f1;
  f2=f2;

proc nlin data=oli converge=0.00000000001;

  parm kk1=0.08 kk2=0.001 kk3=0.05;

    k1=kk1*a1;
    k2=kk2*a2;
    k3=kk3*a3;
    k4=kk4*a4;

model y=(f1*k1/(k3-k1)*exp(-k1*t)+f2*k2/(k3-k2)*exp(-k2*t)-
(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t))**2+
(f1*k1*k3/(k3-k1)/(k4-k1)*exp(-k1*t) +
f2*k2*k3/(k3-k2)/(k4-k2)*exp(-k2*t) -
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t) -
(f1*k1*k3/(k3-k1)/(k4-k1)+f2*k2*k3/(k3-k2)/(k4-k2) -
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2)))*exp(-k4*t))**2;

der.kk1=a1*(2*(f1*k1/(k3-k1)*exp(-k1*t)+f2*k2/(k3-k2)*exp(-k2*t)-
(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t))*(
(f1/(k3-k1)*exp(-k1*t)*(1+k1/(k3-k1)-k1*t)-
f1/(k3-k1)*exp(-k3*t)*(1+k1/(k3-k1))) +
2*((f1*k1*k3/(k3-k1)/(k4-k1)*exp(-k1*t) +
f2*k2*k3/(k3-k2)/(k4-k2)*exp(-k2*t) -
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t) -
(f1*k1*k3/(k3-k1)/(k4-k1)+f2*k2*k3/(k3-k2)/(k4-k2) -
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2)))*exp(-k4*t)))*
(f1*k3/(k3-k1)/(k4-k1)*(1-k1*(2*k1*k3*k4)/(k3-k1)/
(k4-k1))*exp(-k1*t) +
f1*k1*k2/(k3-k1)/(k4-k1)*(-t)*exp(-k1*t) -
k3/(k4-k3)*f1/(k3-k1)*(1+k1/(k3-k1))*exp(-k3*t) -
(f1*k3/(k3-k1)/(k4-k1)*(1-k1*(2*k1*k3*k4)/
(k3-k1)/(k4-k1))-k3/(k4-k3)*f1/(k3-k1)*
(1+k1/(k3-k1)))*exp(-k4*t))),
```

```

der.kk2=a2*(2*(f1*k1/(k3-k1)*exp(-k1*t)+f2*k2/(k3-k2)*exp(-k2*t)-
(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t))*(
(f2/(k3-k2)*exp(-k2*t)*(1+k2/(k3-k2)-k2*t)-
f2/(k3-k2)*exp(-k3*t)*(1+k2/(k3-k2)))+
2*((f1*k1*k3/(k3-k1)/(k4-k1)*exp(-k1*t)-
f2*k2*k3/(k3-k2)/(k4-k2)*exp(-k2*t)-
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t)-
(f1*k1*k3/(k3-k1)/(k4-k1)+f2*k2*k3/(k3-k2)/(k4-k2)-
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2)))*exp(-k4*t))*(
(f2*k3/(k3-k2)/(k4-k2)*(1-k2*(2*k2*k3-k4)/(k3-k2)/
(k4-k2))*exp(-k2*t)-
f2*k2*k3/(k3-k2)/(k4-k2)*(-t)*exp(-k2*t)-
k3/(k4-k3)*f2/(k3-k2)*(1+k2/(k3-k2))*exp(-k3*t)-
(f2*k3/(k3-k2)/(k4-k2)*(1-k2*(2*k2*k3-k4)/
(k3-k2)/(k4-k2))-k3/(k4-k3)*f2/(k3-k2)*
(1+k2/(k3-k2)))*exp(-k4*t)));

```

```

der.kk3=a3*(2*(f1*k1/(k3-k1)*exp(-k1*t)+f2*k2/(k3-k2)*exp(-k2*t)-
(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t))*(
(-f1*k1/(k3-k1)**2*exp(-k1*t)-f2*k2/(k3-k2)**2*exp(-k2*t)-
((f1*k1/(k3-k1)**2+f2*k2/(k3-k2)**2)+(f1*k1/(k3-k1)-
f2*k2/(k3-k2))*(t))*exp(-k3*t))+(
2*((f1*k1*k3/(k3-k1)/(k4-k1)*exp(-k1*t)-
f2*k2*k3/(k3-k2)/(k4-k2)*exp(-k2*t)-
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2))*exp(-k3*t)-
(f1*k1*k3/(k3-k1)/(k4-k1)+f2*k2*k3/(k3-k2)/(k4-k2)-
k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2)))*exp(-k4*t))*(
(f1*k1/(k3-k1)/(k4-k1)*(1-k3/(k3-k1))*exp(-k1*t)-
f2*k2/(k3-k2)/(k4-k2)*(1-k3/(k3-k2))*exp(-k2*t)-
(1/(k4-k3)*(1+k3/(k4-k3))*(f1*k1/(k3-k1)+f2*k2/(k3-k2))-
k3/(k4-k3)*(f1*k1/(k3-k1)**2+f2*k2/(k3-k2)**2))*-
exp(-k3*t)-k3/(k4-k3)*(f1*k1/(k3-k1)+f2*k2/(k3-k2))*-
(-t)*exp(-k3*t)-(f1*k1/(k3-k1)/(k4-k1)*(1-k3/(k3-k1))+
f2*k2/(k3-k2)/(k4-k2)*(1-k3/(k3-k2))-
(1/(k4-k3)*(1+k3/(k4-k3))*(f1*k1/(k3-k1)+f2*k2/(k3-k2))-
k3/(k4-k3)*(f1*k1/(k3-k1)**2+f2*k2/(k3-k2)**2))*-
exp(-k4*t)));

```

run;

```

title 'Modelling Result of CCSM Hydrolysis at 130C'; -- DATA SET ONLY
data oligoaa;
kk4=0.00055;

ff1=0.65;
ff2=1-ff1;

H0=1.39;
f1=ff1*H0;
f2=ff2*H0;

input a t x o;
cards;
0.44   5   .05   .11
0.44   10   .11   .36
0.44   20   .26   .43
0.44   30   .38   .43
0.44   50   .66   .23
0.44   70   .86   .09
0.44   90   .90   .05
0.44   120   1.02   .02
0.44   150   1.10   .0
0.44   180   1.06   .0

0.68   5   .07   .11
0.68   10   .19   .27
0.68   20   .57   .37
0.68   30   .76   .25
0.68   40   .91   .18
0.68   60   1.09   .06
0.68   80   1.14   .02
0.68   100   1.13   .05
0.68   120   1.18   .0
0.68   140   1.19   .0

1.17   4   .08   .13
1.17   8   .31   .30
1.17   12   .65   .30
1.17   16   .83   .18
1.17   20   .94   .08
1.17   30   1.05   .04
1.17   40   1.12   .03
1.17   60   1.16   .02
1.17   80   1.20   .0
1.17   100   1.25   .0

1.90   3   .18   .42
1.90   6   .48   .36
1.90   10   .88   .15
1.90   15   1.06   .0
1.90   20   1.20   .0
1.90   25   1.19   .0
1.90   30   1.18   .0

run;

```

```
title 'Modelling Result of CCSM Hydrolysis at 140c'; -- DATA SET ONLY
```

```
data oligoaa;  
kk4=0.001285;
```

```
ff1=0.65;  
ff2=1-ff1;
```

```
H0=1.39;  
f1=ff1*H0;  
f2=ff2*H0;
```

```
input a t x o;  
cards;
```

```
0.44 5 .09 .22  
0.44 10 .23 .46  
0.44 15 .43 .40  
0.44 20 .62 .32  
0.44 25 .75 .21  
0.44 30 .87 .13  
0.44 40 .98 .05  
0.44 50 1.05 .0  
0.44 70 1.10 .0  
0.44 90 1.15 .0
```

```
0.68 2 .04 .05  
0.68 4 .08 .20  
0.68 7 .28 .45  
0.68 10 .50 .37  
0.68 14 .73 .24  
0.68 18 .90 .14  
0.68 22 1.00 .07  
0.68 30 1.05 .0  
0.68 40 1.11 .0  
0.68 50 1.24 .0
```

```
1.17 2 .07 .07  
1.17 4 .15 .34  
1.17 6 .53 .34  
1.17 8 .79 .20  
1.17 10 .91 .08  
1.17 14 1.07 .0  
1.17 18 1.14 .0  
1.17 22 1.14 .0  
1.17 30 1.19 .0  
1.17 40 1.21 .0
```

```
1.90 2 .10 .13  
1.90 4 .34 .40  
1.90 6 .75 .19  
1.90 8 1.02 .05  
1.90 10 1.07 .04  
1.90 12 1.12 .0  
1.90 14 1.15 .03  
1.90 18 1.17 .02  
1.90 22 1.15 .02
```

```
1.90 30 1.18 .01
```

```
run;
```

```

title 'Modelling Result of CCSM Hydrolysis at 150c'; -- DATA SET ONLY

data oligoaa;
  kk4=0.002917;

  ff1=0.65;
  ff2=1-ff1;

  H0=1.39;
  f1=ff1*H0;
  f2=ff2*H0;

  input a t x o;
  cards;
0.44  2    .06   .08
0.44  4    .12   .35
0.44  7    .35   .55
0.44  10   .55   .48
0.44  14   .80   .37
0.44  18   .93   .24
0.44  22   1.01   .17
0.44  30   1.05   .12
0.44  40   1.12   .07
0.44  50   1.16   .03

0.68  2    .07   .11
0.68  4    .24   .48
0.68  6    .57   .39
0.68  8    .78   .28
0.68  10   .96   .20
0.68  12   1.02   .12
0.68  14   1.03   .09
0.68  20   1.17   .02
0.68  30   1.12   .02
0.68  40   1.17   .0

1.17  1    .08   .01
1.17  2    .09   .10
1.17  3    .26   .34
1.17  4    .60   .34
1.17  6    .97   .09
1.17  8    1.10   .02
1.17  10   1.16   .0
1.17  15   1.16   .0
1.17  20   1.24   .0
1.17  30   1.23   .0

1.90  1    .08   .07
1.90  2    .10   .29
1.90  3    .29   .50
1.90  4    .67   .31
1.90  5    .99   .13
1.90  6    1.09   .07
1.90  8    1.13   .03
1.90  10   1.17   .02
1.90  20   1.09   .07

```

run;

Appendix 5.

Modeling Results of Corn Cobs/Stover Mixture Hydrolysis

Modelling Result of CCSM Hydrolysis at 120c 459
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.080000	0.001000	0.050000	0.534297
1	0.073875	0.004109	0.042546	0.146299
2	0.068823	0.004492	0.045310	0.126837
3	0.067543	0.004536	0.045087	0.124052
4	0.066852	0.004530	0.045237	0.122888
5	0.066495	0.004534	0.045221	0.122348
6	0.066289	0.004534	0.045244	0.122069
7	0.066173	0.004534	0.045245	0.121919
8	0.066105	0.004534	0.045249	0.121834

Modelling Result of CCSM Hydrolysis at 120c 460
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
9	0.066065	0.004535	0.045251	0.121786
10	0.066042	0.004535	0.045252	0.121758
11	0.066028	0.004535	0.045252	0.121742
12	0.066020	0.004535	0.045253	0.121732
13	0.066015	0.004535	0.045253	0.121726
14	0.066012	0.004535	0.045253	0.121723
15	0.066011	0.004535	0.045253	0.121721
16	0.066010	0.004535	0.045253	0.121720
17	0.066009	0.004535	0.045253	0.121719

Modelling Result of CCSM Hydrolysis at 120c 461
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
18	0.066009	0.004535	0.045253	0.121719
19	0.066008	0.004535	0.045253	0.121718
20	0.066008	0.004535	0.045253	0.121718
21	0.066008	0.004535	0.045253	0.121718
22	0.066008	0.004535	0.045253	0.121718
23	0.066008	0.004535	0.045253	0.121718
24	0.066008	0.004535	0.045253	0.121718
25	0.066008	0.004535	0.045253	0.121718
26	0.066008	0.004535	0.045253	0.121718

Modelling Result of CCSM Hydrolysis at 120c 462
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
27	0.066008	0.004535	0.045253	0.121718
28	0.066008	0.004535	0.045253	0.121718
29	0.066008	0.004535	0.045253	0.121718
30	0.066008	0.004535	0.045253	0.121718
31	0.066008	0.004535	0.045253	0.121718
32	0.066008	0.004535	0.045253	0.121718
33	0.066008	0.004535	0.045253	0.121718
34	0.066008	0.004535	0.045253	0.121718

NOTE: Convergence criterion met.

Modelling Result of CCSM Hydrolysis at 120c 463
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	14.483932202	4.827977401
Residual	33	0.121718038	0.003688425
Uncorrected Total	36	14.605650240	
(Corrected Total)	35	4.426998080	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval	
			Lower	Upper
KK1	0.0660082051	0.00161421390	0.06272408344	0.06929232671
KK2	0.0045348395	0.00049279944	0.00353223801	0.00553744103
KK3	0.0452532258	0.00404495106	0.03702376417	0.05348268737

Modelling Result of Corn/Stover Hydrolysis at 120c 464
 14:36 Monday, June 6, 1994

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	-0.074108688	-0.317356156
KK2	-0.074108688	1	-0.681738779
KK3	-0.317356156	-0.681738779	1

Modelling Result of CCSM Hydrolysis at 130c 424
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.150000	0.005000	0.100000	2.800598
1	0.157633	0.011885	0.154122	0.626252
2	0.157483	0.014123	0.141852	0.564465
3	0.156129	0.014243	0.144999	0.562423
4	0.154940	0.014170	0.151648	0.562139
5	0.154837	0.014244	0.147424	0.561628
6	0.154769	0.014231	0.148474	0.561596
7	0.154775	0.014248	0.147775	0.561591
8	0.154705	0.014229	0.148922	0.561588

Modelling Result of CCSM Hydrolysis at 130c 425
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
9	0.154720	0.014245	0.147954	0.561565
10	0.154682	0.014235	0.148591	0.561560
11	0.154691	0.014244	0.148051	0.561552
12	0.154667	0.014238	0.148408	0.561547
13	0.154671	0.014243	0.148105	0.561544
14	0.154655	0.014240	0.148305	0.561539
15	0.154657	0.014246	0.147962	0.561538
16	0.154627	0.014236	0.148528	0.561532
17	0.154637	0.014244	0.148050	0.561528

Modelling Result of CCSM Hydrolysis at 130c 426
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
18	0.154618	0.014239	0.148367	0.561523
19	0.154623	0.014243	0.148099	0.561523
20	0.154611	0.014240	0.148277	0.561519
21	0.154613	0.014243	0.148126	0.561518
22	0.154604	0.014241	0.148225	0.561515
23	0.154605	0.014244	0.148054	0.561515
24	0.154591	0.014240	0.148336	0.561510
25	0.154593	0.014242	0.148217	0.561510
26	0.154594	0.014244	0.148058	0.561510

Modelling Result of CCSM Hydrolysis at 130c 427
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
 Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
27	0.154581	0.014240	0.148321	0.561506
28	0.154583	0.014242	0.148210	0.561505
29	0.154584	0.014243	0.148136	0.561505
30	0.154579	0.014242	0.148185	0.561503
31	0.154579	0.014244	0.148101	0.561503
32	0.154571	0.014241	0.148238	0.561500
33	0.154571	0.014242	0.148224	0.561500

NOTE: Convergence criterion met.

Modelling Result of CCSM Hydrolysis at 130c 428
 14:36 Monday, June 6, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	33.785603811	11.261867937
Residual	34	0.561500259	0.016514714
Uncorrected Total	37	34.347104070	
(Corrected Total)	36	9.026677432	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval	
			Lower	Upper
KK1	0.1545714864	0.00051773888	0.15351932091	0.15562365185
KK2	0.0142415062	0.00142334347	0.01134894217	0.01713407019
KK3	0.1482238746	0.02629897793	0.09477825264	0.20166949655

Modelling Result of Corn/Stover Hydrolysis at 130c 429
 14:36 Monday, June 6, 1994

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	0.1102802912	-0.388784289
KK2	0.1102802912	1	-0.559383798
KK3	-0.388784289	-0.559383798	1

Modelling Result of CCSM Hydrolysis at 140c 633
14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
0	0.210000	0.011000	0.100000	6.187966
1	0.328857	0.018991	0.223631	1.086162
2	0.262049	0.028630	0.325897	0.319071
3	0.264762	0.031457	0.309132	0.306183
4	0.264439	0.031822	0.293827	0.302417
5	0.263867	0.031867	0.287667	0.301908
6	0.263664	0.031813	0.288580	0.301651
7	0.263377	0.031816	0.288773	0.301353
8	0.263050	0.031812	0.289152	0.301005

Modelling Result of CCSM Hydrolysis at 140c 634
14:36 Monday, June 6, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable Y Method: Gauss-Newton

Iter	KK1	KK2	KK3	Sum of Squares
9	0.262666	0.031809	0.289597	0.300598
10	0.262217	0.031804	0.290160	0.300121
11	0.261691	0.031798	0.290886	0.299561
12	0.261075	0.031789	0.291854	0.298903
13	0.260362	0.031776	0.293194	0.298138
14	0.259566	0.031757	0.295112	0.297282
15	0.258749	0.031729	0.297877	0.296434
16	0.258071	0.031692	0.301612	0.295874
17	0.258053	0.031689	0.301874	0.295874

NOTE: Convergence criterion met.

Modelling Result of CCSM Hydrolysis at 140c 635
14:36 Monday, June 6, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	35.708592075	11.902864025
Residual	37	0.295873585	0.007996583
Uncorrected Total	40	36.004465660	
(Corrected Total)	39	9.489554104	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval	
			Lower	Upper
KK1	0.2580529920	0.00037338998	0.25729643608	0.25880954785
KK2	0.0316893720	0.00221765061	0.02719600925	0.03618273473
KK3	0.3018744495	0.03534676817	0.23025548028	0.37349341872

Modelling Result of Corn/Stover Hydrolysis at 140c

636

14:36 Monday, June 6, 1994

Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	0.0893693271	-0.34258612
KK2	0.0893693271	1	-0.611114557
KK3	-0.34258612	-0.611114557	1

Modelling Result of CCSM Hydrolysis at 150c 37
 23:38 Tuesday, June 7, 1994

Iter	Non-Linear Least Squares Iterative Phase		
	Dependent Variable Y	Method: Gauss-Newton	
0	KK1 0.280000	KK2 0.050000	KK3 0.160000
1	0.478368	0.045199	0.272419
2	0.445836	0.046290	0.513032
3	0.448865	0.054513	0.611575
4	0.442321	0.055953	0.570852
5	0.441916	0.055995	0.569733
6	0.441714	0.056016	0.569201

NOTE: Convergence criterion met.

Modelling Result of CCSM Hydrolysis at 150c 38
 23:38 Tuesday, June 7, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable Y

Source	DF	Sum of Squares	Mean Square
Regression	3	34.807938649	11.602646216
Residual	36	0.828791311	0.023021981
Uncorrected Total	39	35.636729960	
(Corrected Total)	38	9.834217836	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic Confidence Interval	95 % Lower	Upper
KK1	0.4417136434	0.01596667362	0.40933191177	0.47409537493	
KK2	0.0560155307	0.00700066359	0.04181760724	0.07021345408	
KK3	0.5692010776	0.14801171783	0.26902110085	0.86938105434	

Modelling Result of Corn/Stover Hydrolysis at 150c 39
 23:38 Tuesday, June 7, 1994

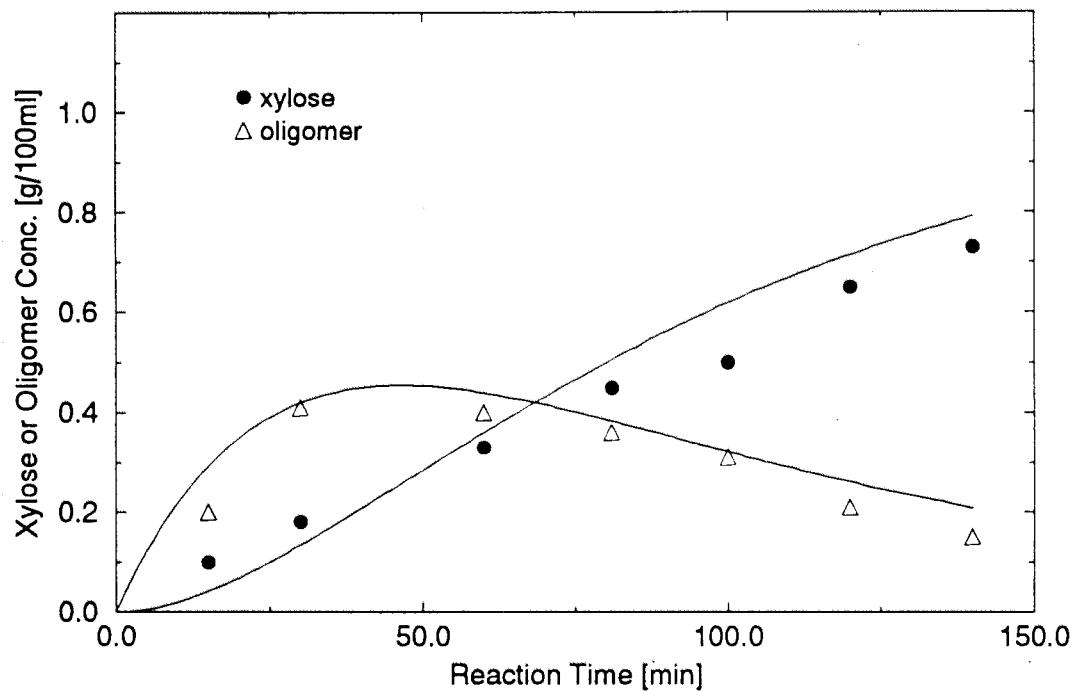
Asymptotic Correlation Matrix

Corr	KK1	KK2	KK3
KK1	1	-0.168824362	0.6497089615
KK2	-0.168824362	1	-0.570281879
KK3	0.6497089615	-0.570281879	1

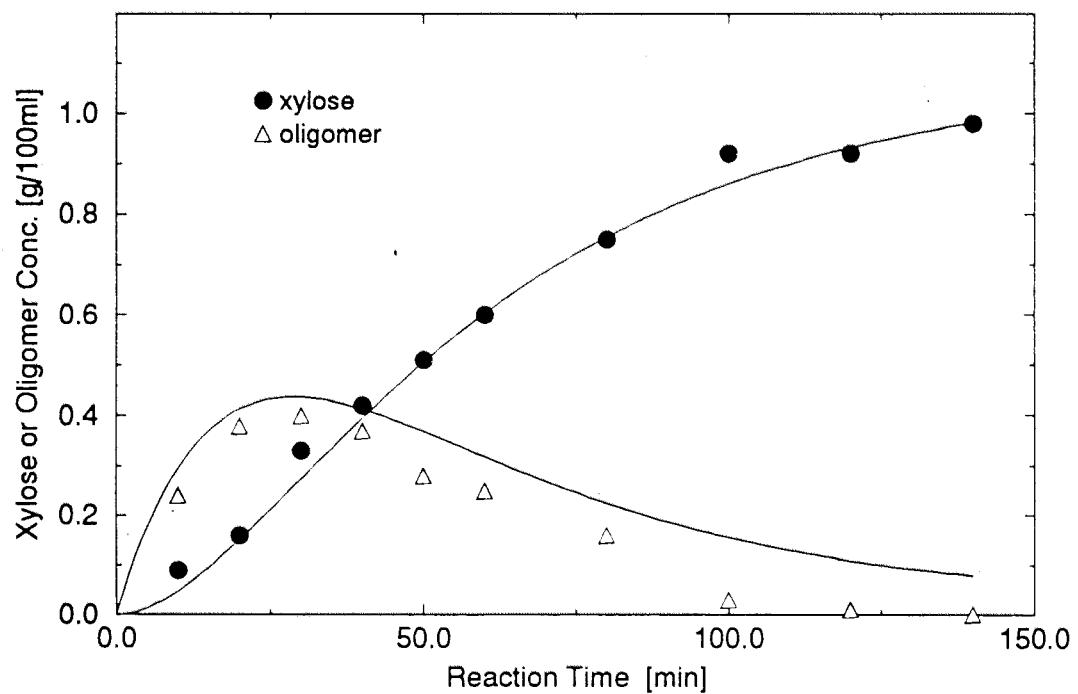
Appendix 6.

Comparison Between Experimental and Model Values for Reaction Progression in Hydrolysis of Corn Cobs/Stover Mixture

Reaction Progression in CCSM Hydrolysis at 120c
(Acid Conc=0.44%, Solid:Liquid=1:16.4)



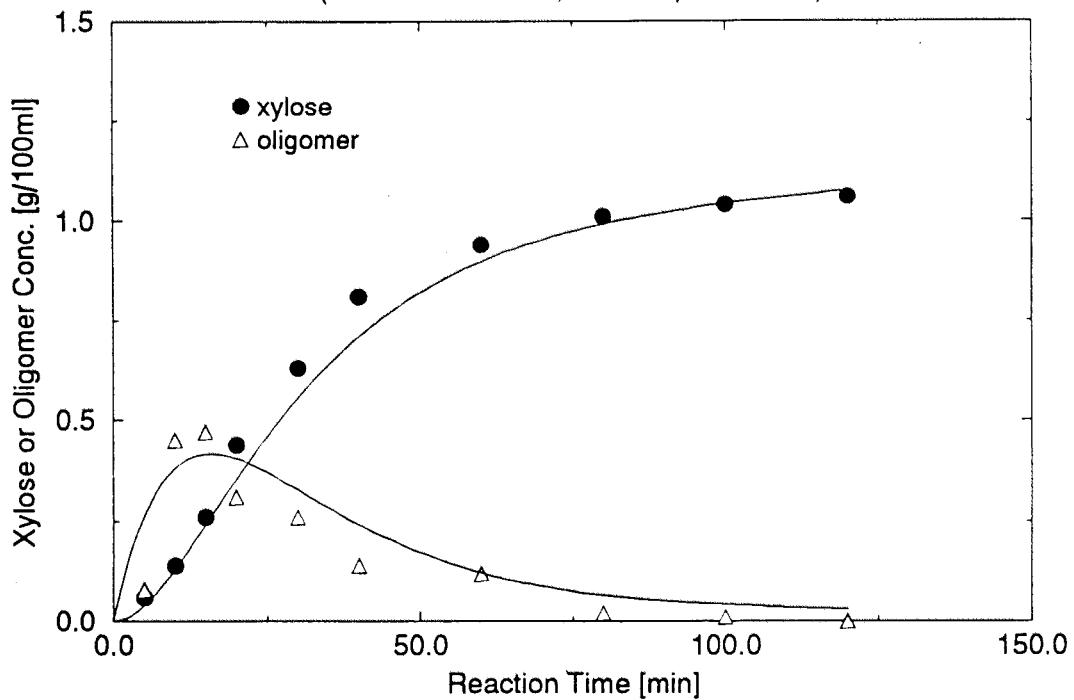
(Acid Conc=0.68%, Solid:Liquid=1:16.4)



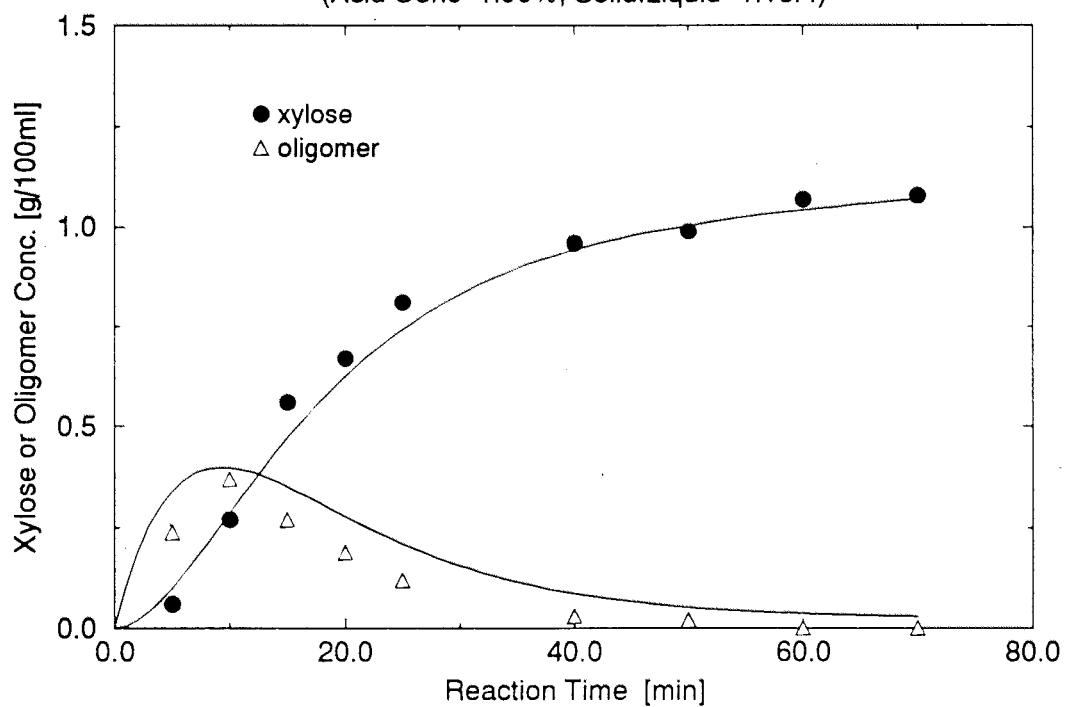
(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 120c

(Acid Conc=1.17%, Solid:Liquid=1:16.4)

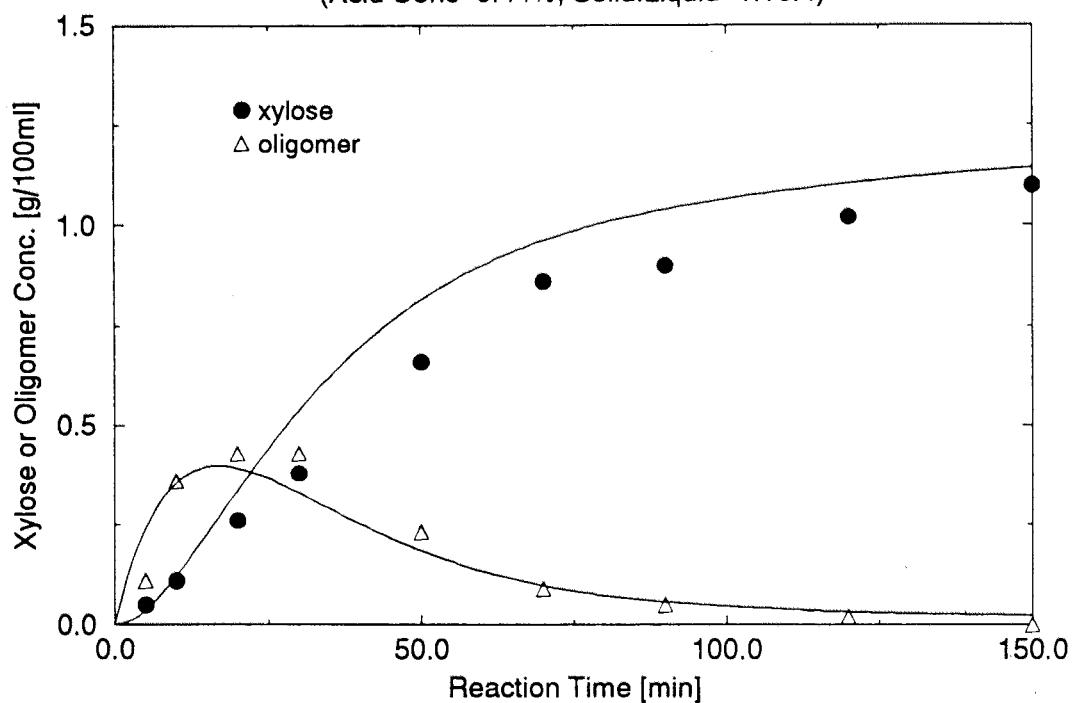


(Acid Conc=1.90%, Solid:Liquid=1:16.4)

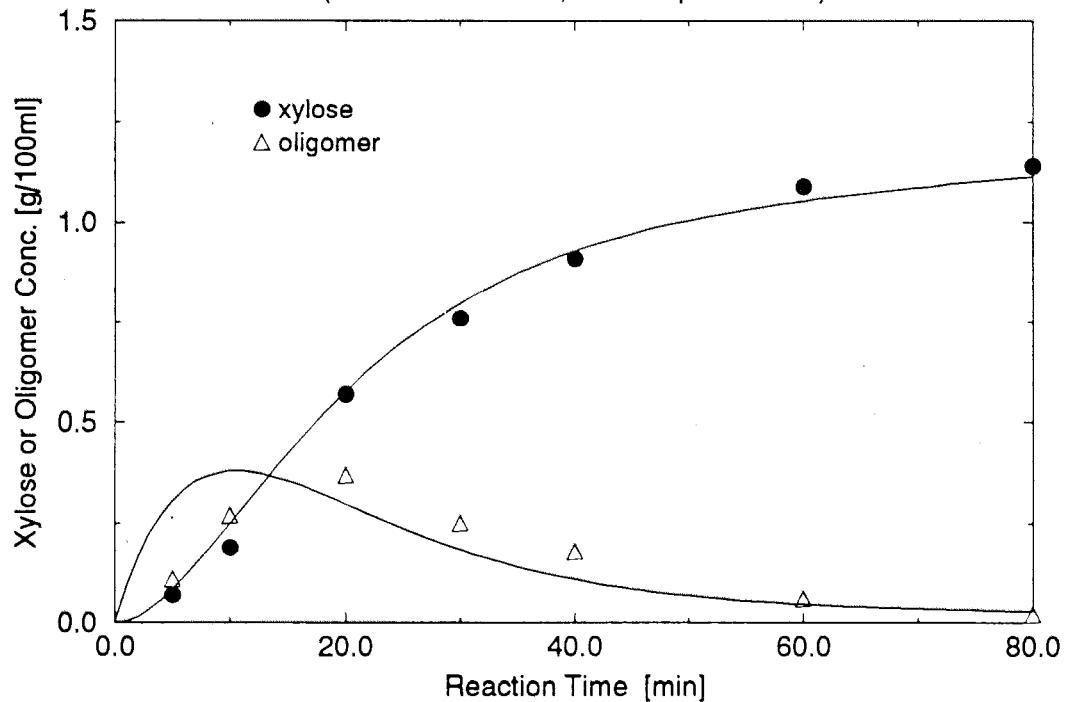


(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 130c
(Acid Conc=0.44%, Solid:Liquid=1:16.4)



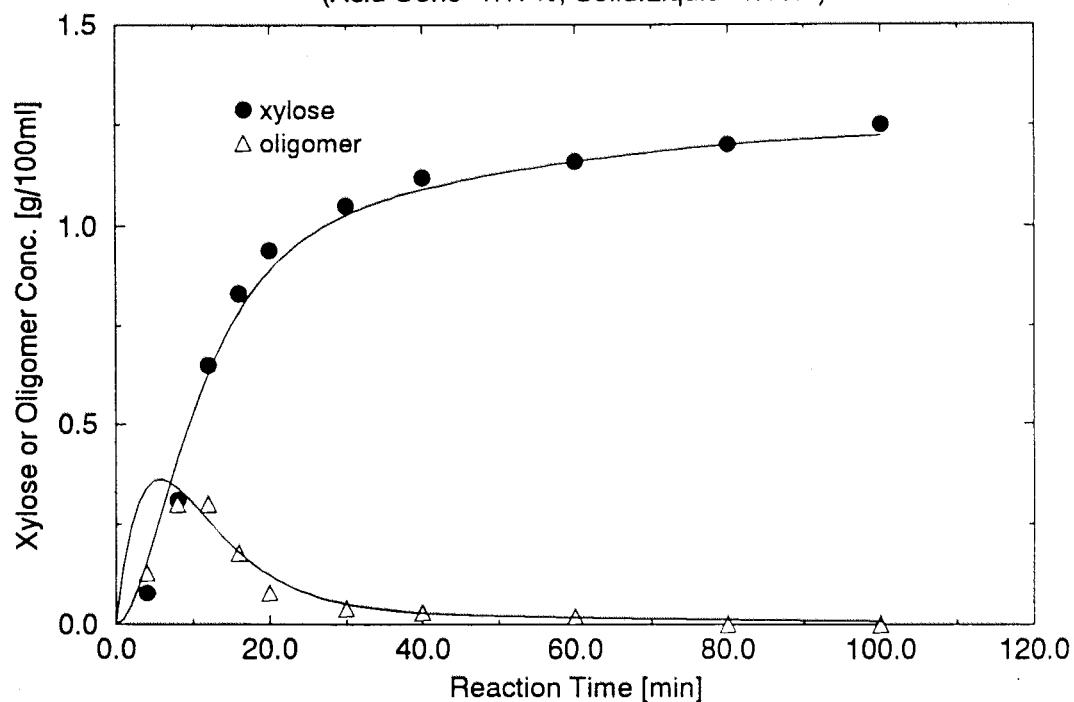
(Acid Conc=0.68%, Solid:Liquid=1:16.4)



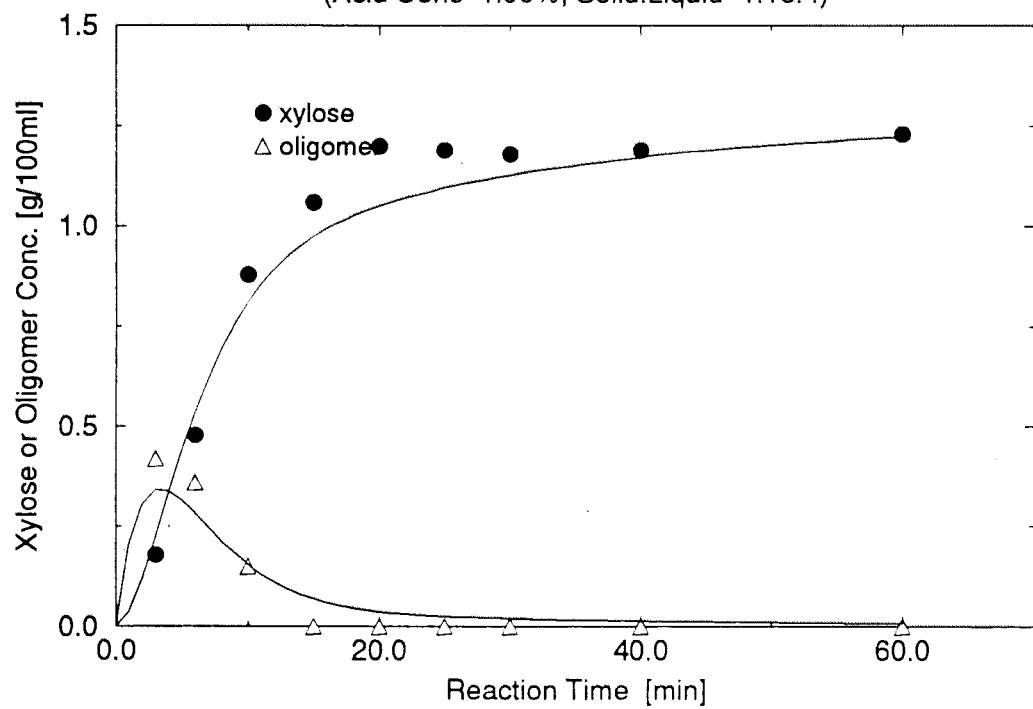
(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 130c

(Acid Conc=1.17%, Solid:Liquid=1:16.4)



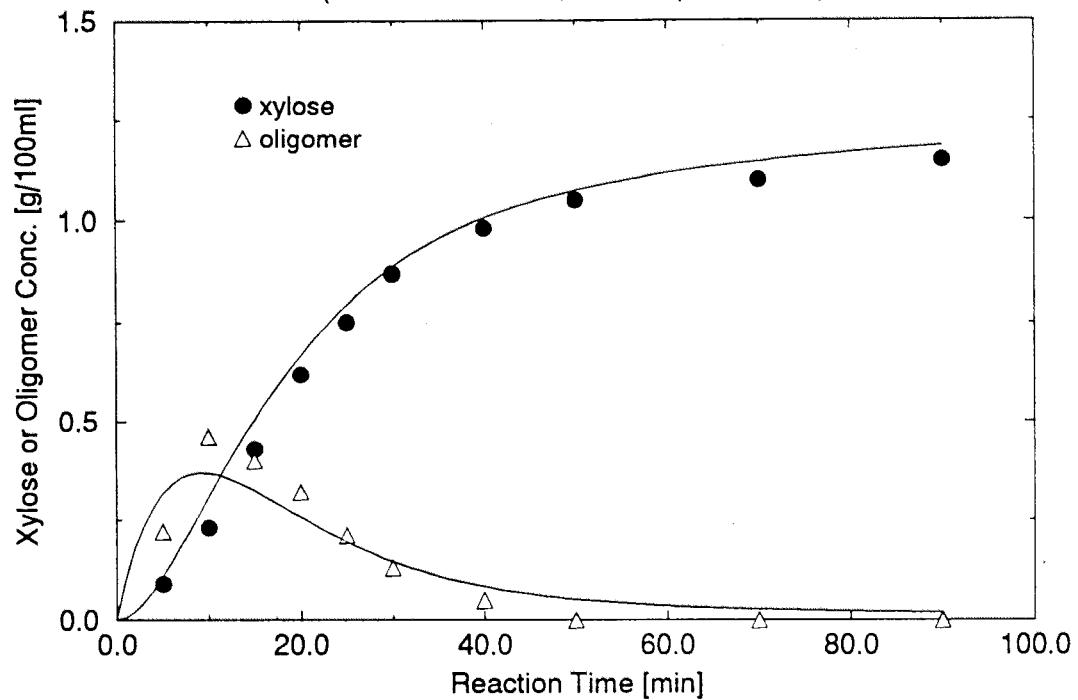
(Acid Conc=1.90%, Solid:Liquid=1:16.4)



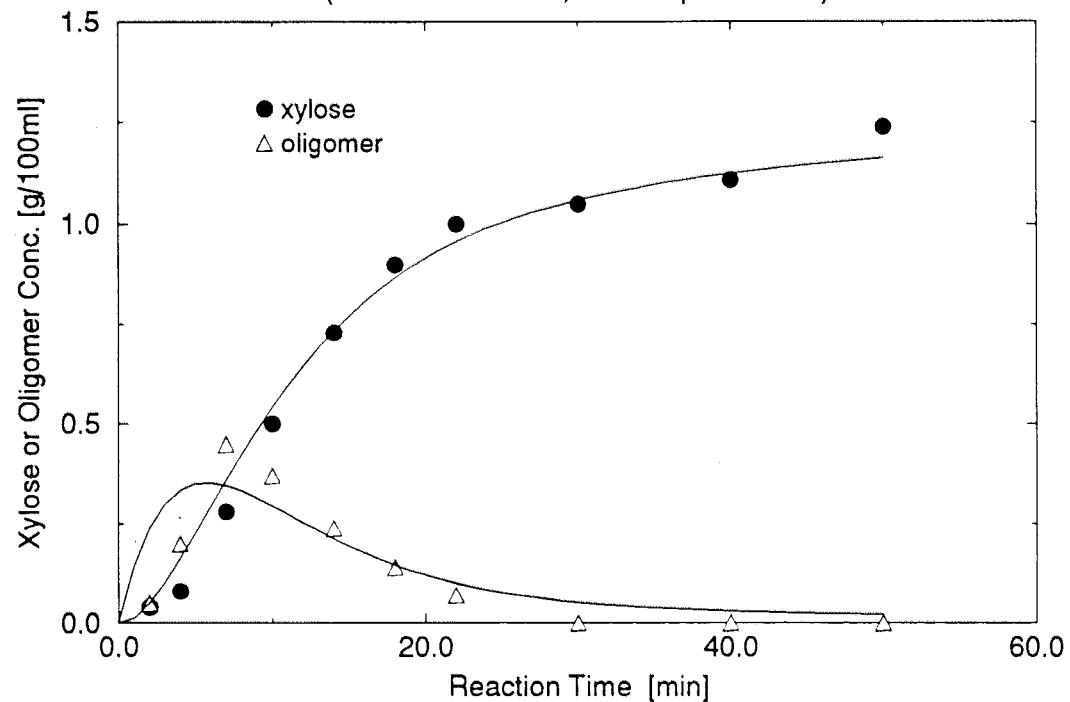
(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 140c

(Acid Conc=0.44%, Solid:Liquid=1:16.4)



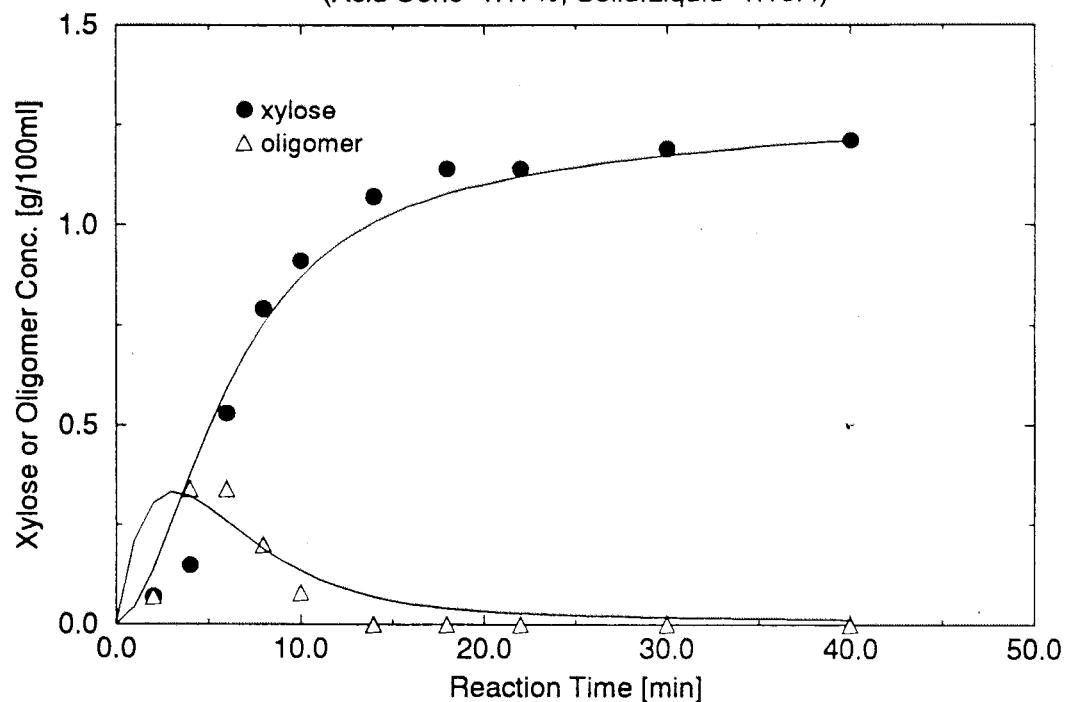
(Acid Conc=0.68%, Solid:Liquid=1:16.4)



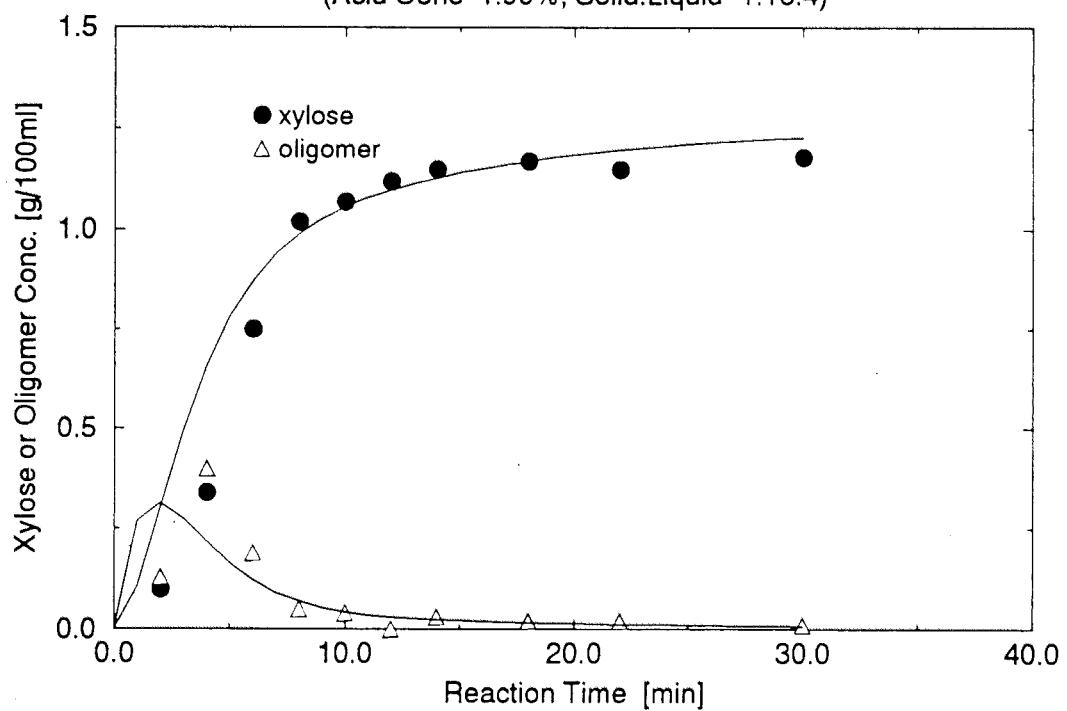
(--: Best Fit for Individual Run)

Reaction Progression in CCMS Hydrolysis at 140c

(Acid Conc=1.17%, Solid:Liquid=1:16.4)

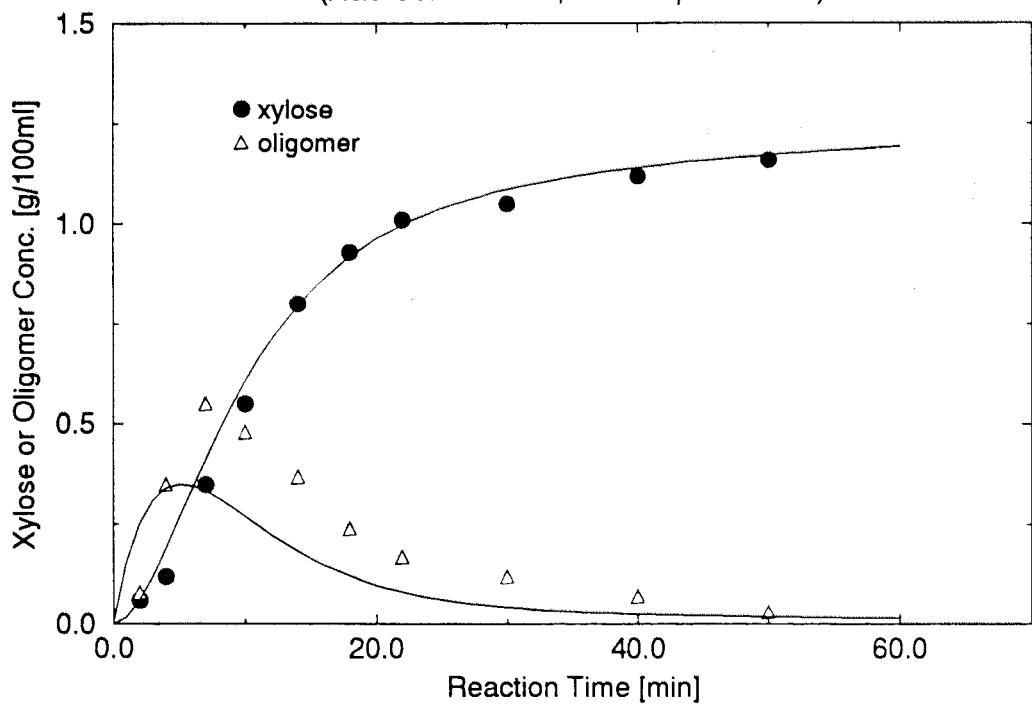


(Acid Conc=1.90%, Solid:Liquid=1:16.4)

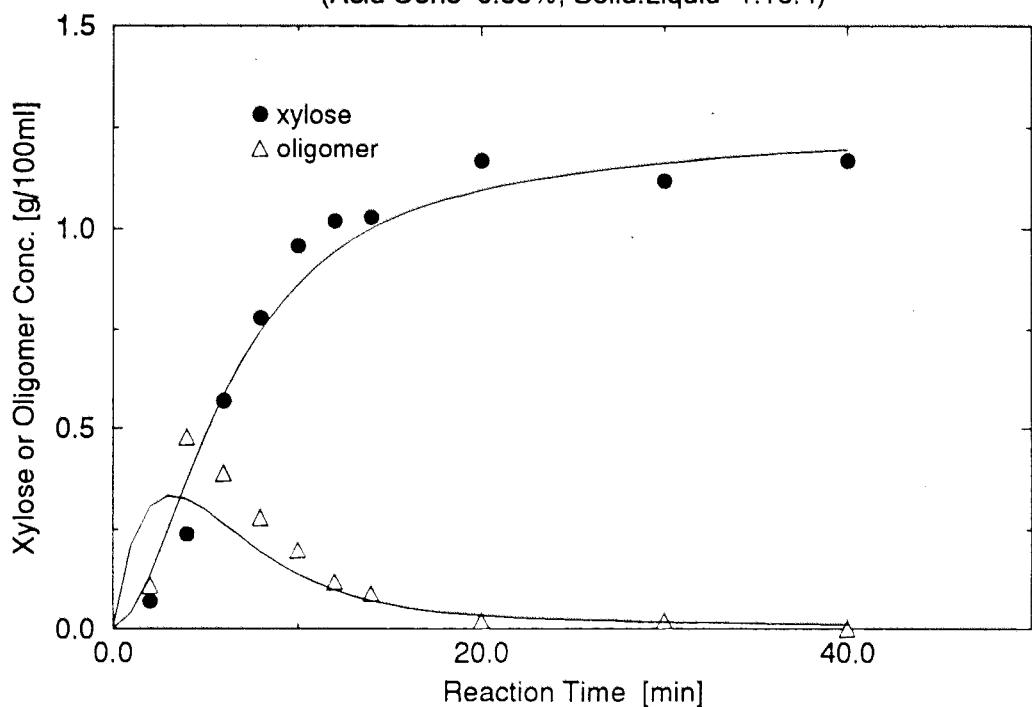


(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 150c
(Acid Conc=0.44%, Solid:Liquid=1:16.4)



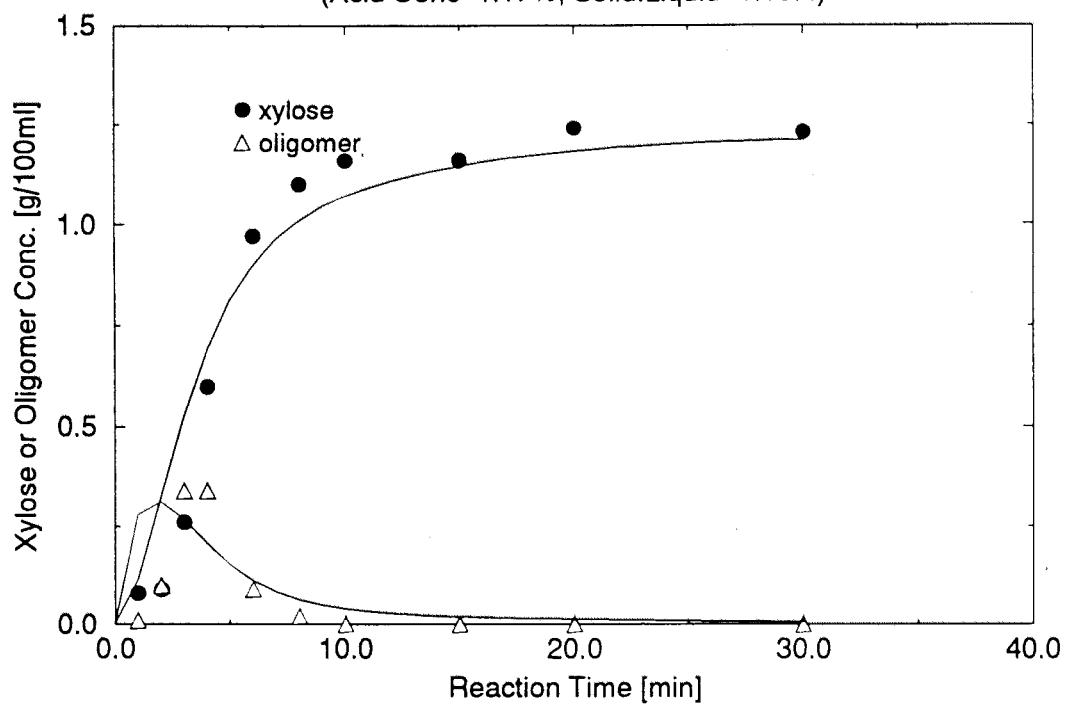
(Acid Conc=0.68%, Solid:Liquid=1:16.4)



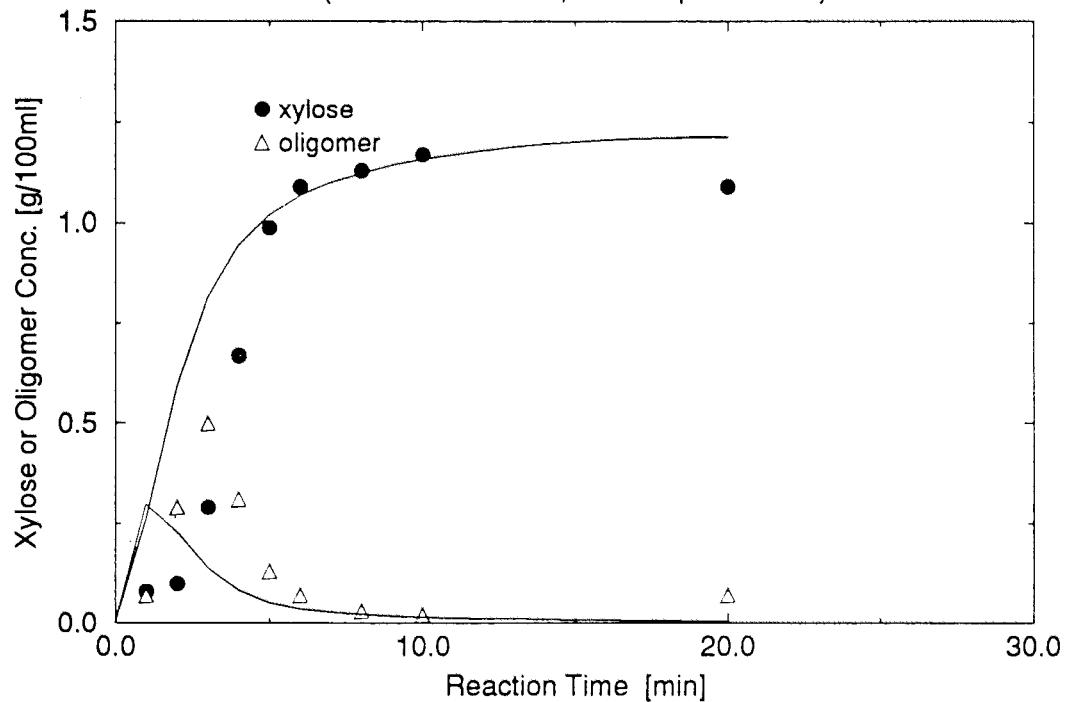
(--: Best Fit for Individual Run)

Reaction Progression in CCSM Hydrolysis at 150c

(Acid Conc=1.17%, Solid:Liquid=1:16.4)



(Acid Conc=1.90%, Solid:Liquid=1:16.4)



(--: Best Fit for Individual Run)

Appendix 7.

SAS Programs with Raw Data for Determination of

Thermal Diffusivities of Biomass Feedstocks

```
title 'Thermal Diffusivity for Hybrid Poplar Bark';
```

```
data ht;
```

```
  n0=3.1415926/2;
```

```
  n1=3*n0;
```

```
  n2=5*n0;
```

```
  n3=7*n0;
```

```
  n4=9*n0;
```

```
  n5=11*n0;
```

```
  n6=13*n0;
```

```
  n7=15*n0;
```

```
  L=1.3;
```

```
  input ti T To Ts;
```

```
  cards;
```

```
0     8.4   8.4   30.5
```

```
15    9.1   8.4   30.5
```

```
30    9.6   8.4   30.5
```

```
45    10.0  8.4   30.5
```

```
60    10.4  8.4   30.5
```

```
75    10.9  8.4   30.5
```

```
90    11.3  8.4   30.5
```

```
120   12.2  8.4   30.5
```

```
150   12.8  8.4   30.5
```

```
180   13.6  8.4   30.5
```

```
210   14.2  8.4   30.5
```

```
240   14.8  8.4   30.5
```

```
270   15.4  8.4   30.5
```

```
300   16.0  8.4   30.5
```

```
330   16.5  8.4   30.5
```

```
360   17.1  8.4   30.5
```

```
390   17.6  8.4   30.5
```

```
420   18.1  8.4   30.5
```

```
450   18.6  8.4   30.5
```

```
480   19.0  8.4   30.5
```

```
510   19.5  8.4   30.5
```

```
540   19.9  8.4   30.5
```

```
570   20.3  8.4   30.5
```

```
600   20.7  8.4   30.5
```

```
660   21.5  8.4   30.5
```

```
690   21.8  8.4   30.5
```

```
720   22.1  8.4   30.5
```

```
780   22.7  8.4   30.5
```

```
840   23.4  8.4   30.5
```

```
900   23.9  8.4   30.5
```

```
960   24.6  8.4   30.5
```

```
1020  25.1  8.4   30.5
```

```
1080  25.6  8.4   30.5
```

```
1200  26.4  8.4   30.5
```

```
1320  27.1  8.4   30.5
```

```
1440  27.6  8.4   30.5
```

```
1560  28.1  8.4   30.5
```

```
1680  28.5  8.4   30.5
```

```
1800  28.9  8.4   30.5
```

```
1980  29.3  8.4   30.5
```

```
2160  29.6  8.4   30.5
```

```
2400  29.9  8.4   30.5
```

```
2700  30.1  8.4   30.5
```

```
3000  30.2  8.4   30.5
```

```
3300  30.3  8.4   30.5
```

```
3600  30.4  8.4   30.5
```

```
4200  30.5  8.4   30.5
```

```
/*
```

0	5.7	5.7	44.2
15	6.5	5.7	44.2
30	7.5	5.7	44.2
60	8.4	5.7	44.2
75	9.1	5.7	44.2
90	9.8	5.7	44.2
105	10.7	5.7	44.2
120	11.5	5.7	44.2
135	12.3	5.7	44.2
150	13.0	5.7	44.2
165	13.8	5.7	44.2
180	14.5	5.7	44.2
210	15.9	5.7	44.2
225	16.6	5.7	44.2
240	17.1	5.7	44.2
270	18.3	5.7	44.2
300	19.5	5.7	44.2
330	20.9	5.7	44.2
360	21.6	5.7	44.2
390	22.6	5.7	44.2
420	23.5	5.7	44.2
450	24.4	5.7	44.2
480	25.3	5.7	44.2
510	26.2	5.7	44.2
540	27.1	5.7	44.2
570	27.9	5.7	44.2
600	28.7	5.7	44.2
630	29.3	5.7	44.2
660	30.0	5.7	44.2
720	31.3	5.7	44.2
780	32.4	5.7	44.2
840	33.5	5.7	44.2
900	34.5	5.7	44.2
960	35.4	5.7	44.2
1020	36.2	5.7	44.2
1080	37.0	5.7	44.2
1140	37.6	5.7	44.2
1200	38.2	5.7	44.2
1320	39.3	5.7	44.2
1470	40.4	5.7	44.2
1620	41.2	5.7	44.2
1800	42.0	5.7	44.2
2100	42.8	5.7	44.2
2400	43.4	5.7	44.2
2700	43.8	5.7	44.2
3000	43.9	5.7	44.2
3300	44.1	5.7	44.2
3600	44.2	5.7	44.2

0	23.3	23.3	63.5
15	25.1	23.3	63.5
30	26.2	23.3	63.5
45	27.8	23.3	63.5
60	29.2	23.3	63.5
75	30.6	23.3	63.5
90	31.7	23.3	63.5
105	32.8	23.3	63.5
120	33.8	23.3	63.5
135	34.7	23.3	63.5
150	35.5	23.3	63.5
165	36.2	23.3	63.5
180	37.0	23.3	63.5
195	37.8	23.3	63.5
210	38.5	23.3	63.5
225	39.1	23.3	63.5
240	39.8	23.3	63.5

255	40.5	23.3	63.5
270	41.1	23.3	63.5
285	41.7	23.3	63.5
300	42.3	23.3	63.5
315	42.9	23.3	63.5
345	43.9	23.3	63.5
360	44.4	23.3	63.5
390	45.4	23.3	63.5
420	46.3	23.3	63.5
450	46.9	23.3	63.5
480	47.6	23.3	63.5
510	48.2	23.3	63.5
540	48.8	23.3	63.5
570	49.4	23.3	63.5
600	49.9	23.3	63.5
630	50.4	23.3	63.5
660	50.9	23.3	63.5
690	51.5	23.3	63.5
720	52.2	23.3	63.5
780	53.4	23.3	63.5
840	54.5	23.3	63.5
960	56.3	23.3	63.5
1080	57.8	23.3	63.5
1200	59.0	23.3	63.5
1320	60.0	23.3	63.5
1440	60.6	23.3	63.5
1620	61.5	23.3	63.5
1800	62.0	23.3	63.5
2100	62.5	23.3	63.5
2400	62.8	23.3	63.5
2760	62.9	23.3	63.5
2880	63.0	23.3	63.5

0	25.6	25.6	77.4
15	27.5	25.6	77.4
30	29.3	25.6	77.4
45	31.0	25.6	77.4
60	32.7	25.6	77.4
75	34.9	25.6	77.4
90	36.7	25.6	77.4
105	38.3	25.6	77.4
120	39.7	25.6	77.4
135	40.9	25.6	77.4
150	42.1	25.6	77.4
165	43.2	25.6	77.4
180	44.3	25.6	77.4
195	45.3	25.6	77.4
210	46.2	25.6	77.4
225	47.1	25.6	77.4
240	48.1	25.6	77.4
255	48.3	25.6	77.4
270.	49.2	25.6	77.4
285	50.0	25.6	77.4
300	50.9	25.6	77.4
315	51.7	25.6	77.4
330	52.5	25.6	77.4
360	53.3	25.6	77.4
390	54.2	25.6	77.4
420	55.5	25.6	77.4
450	56.4	25.6	77.4
480	57.6	25.6	77.4
510	58.9	25.6	77.4
540	60.6	25.6	77.4
570	61.1	25.6	77.4
600	62.2	25.6	77.4
630	63.0	25.6	77.4

660	64.0	25.6	77.4
690	65.0	25.6	77.4
720	65.8	25.6	77.4
750	66.7	25.6	77.4
780	67.5	25.6	77.4
810	67.9	25.6	77.4
840	68.6	25.6	77.4
900	69.8	25.6	77.4
960	71.0	25.6	77.4
1020	71.9	25.6	77.4
1080	72.8	25.6	77.4
1140	73.5	25.6	77.4
1200	74.2	25.6	77.4
1260	74.8	25.6	77.4
1320	75.2	25.6	77.4
1440	75.9	25.6	77.4
1560	76.5	25.6	77.4
1680	76.9	25.6	77.4
1800	77.1	25.6	77.4
1920	77.2	25.6	77.4
2040	77.3	25.6	77.4

0	26.4	26.4	86.0
15	27.0	26.4	86.0
30	28.9	26.4	86.0
45	30.8	26.4	86.0
60	32.4	26.4	86.0
75	34.3	26.4	86.0
90	36.4	26.4	86.0
105	38.1	26.4	86.0
120	39.9	26.4	86.0
135	41.7	26.4	86.0
150	43.4	26.4	86.0
165	45.0	26.4	86.0
180	46.4	26.4	86.0
195	48.1	26.4	86.0
210	49.4	26.4	86.0
225	50.9	26.4	86.0
240	52.2	26.4	86.0
255	53.5	26.4	86.0
270	54.9	26.4	86.0
285	56.1	26.4	86.0
300	57.4	26.4	86.0
330	59.6	26.4	86.0
345	60.7	26.4	86.0
360	61.7	26.4	86.0
375	62.6	26.4	86.0
390	63.5	26.4	86.0
420	65.3	26.4	86.0
450	66.9	26.4	86.0
480	68.5	26.4	86.0
510.	69.8	26.4	86.0
540.	71.2	26.4	86.0
570	72.3	26.4	86.0
600	73.4	26.4	86.0
630	74.4	26.4	86.0
660	75.4	26.4	86.0
690	76.2	26.4	86.0
720	77.1	26.4	86.0
780	78.6	26.4	86.0
840	79.7	26.4	86.0
900	80.7	26.4	86.0
960	81.6	26.4	86.0
1020	82.4	26.4	86.0
1080	82.9	26.4	86.0
1200	83.9	26.4	86.0

```

1380 84.8 26.4 86.0
1560 85.5 26.4 86.0
1800 85.8 26.4 86.0
1980 85.9 26.4 86.0
2100 86.0 26.4 86.0
*/
run;

data dim;
  set ht;

theta=(T-Ts) / (To-Ts);

run;

proc nlin data=dim converge=0.0000000001;
  parm alpha=0.001;

  model theta=2*(exp(-n0**2*alpha*ti/L**2)/n0
    -exp(-n1**2*alpha*ti/L**2)/n1
    +exp(-n2**2*alpha*ti/L**2)/n2
    -exp(-n3**2*alpha*ti/L**2)/n3
    +exp(-n4**2*alpha*ti/L**2)/n4
    -exp(-n5**2*alpha*ti/L**2)/n5
    +exp(-n6**2*alpha*ti/L**2)/n6
    -exp(-n7**2*alpha*ti/L**2)/n7);

/*
der.alpha=2*(exp(-n0**2*alpha*ti/L**2)/n0*(-n0**2*alpha/L**2)
  -exp(-n1**2*alpha*ti/L**2)/n1*(-n1**2*alpha/L**2)
  +exp(-n2**2*alpha*ti/L**2)/n2*(-n2**2*alpha/L**2)
  -exp(-n3**2*alpha*ti/L**2)/n3*(-n3**2*alpha/L**2)
  +exp(-n4**2*alpha*ti/L**2)/n4*(-n4**2*alpha/L**2)
  -exp(-n5**2*alpha*ti/L**2)/n5*(-n5**2*alpha/L**2)
  +exp(-n6**2*alpha*ti/L**2)/n6*(-n6**2*alpha/L**2)
  -exp(-n7**2*alpha*ti/L**2)/n7*(-n7**2*alpha/L**2));
*/
run;

```

```
title 'Thermal Diffusivity in for Switchgrass';
```

```
data ht;
```

```
  n0=3.1415926/2;
```

```
  n1=3*n0;
```

```
  n2=5*n0;
```

```
  n3=7*n0;
```

```
  n4=9*n0;
```

```
  n5=11*n0;
```

```
  n6=13*n0;
```

```
  n7=15*n0;
```

```
  L=1.3;
```

```
  input ti T To Ts;
```

```
  cards;
```

```
 0   6.1   6.1   30.4
```

```
 15  6.2   6.1   30.4
```

```
 30  6.7   6.1   30.4
```

```
 45  7.0   6.1   30.4
```

```
 60  7.2   6.1   30.4
```

```
 90  7.7   6.1   30.4
```

```
 120 8.2   6.1   30.4
```

```
 150 8.7   6.1   30.4
```

```
 180 9.3   6.1   30.4
```

```
 210 9.8   6.1   30.4
```

```
 240 10.4   6.1   30.4
```

```
 270 10.8   6.1   30.4
```

```
 300 11.4   6.1   30.4
```

```
 330 11.9   6.1   30.4
```

```
 360 12.4   6.1   30.4
```

```
 390 12.9   6.1   30.4
```

```
 420 13.4   6.1   30.4
```

```
 450 13.9   6.1   30.4
```

```
 480 14.5   6.1   30.4
```

```
 510 15.0   6.1   30.4
```

```
 540 15.5   6.1   30.4
```

```
 570 15.9   6.1   30.4
```

```
 600 16.4   6.1   30.4
```

```
 630 16.8   6.1   30.4
```

```
 660 17.3   6.1   30.4
```

```
 690 17.7   6.1   30.4
```

```
 720 18.0   6.1   30.4
```

```
 780 18.8   6.1   30.4
```

```
 840 19.6   6.1   30.4
```

```
 900 20.4   6.1   30.4
```

```
 960 21.1   6.1   30.4
```

```
 1020 21.8   6.1   30.4
```

```
 1080 22.3   6.1   30.4
```

```
 1140 22.9   6.1   30.4
```

```
 1200 23.4   6.1   30.4
```

```
 1320 24.3   6.1   30.4
```

```
 1440 25.2   6.1   30.4
```

```
 1560 26.0   6.1   30.4
```

```
 1680 26.7   6.1   30.4
```

```
 1800 27.1   6.1   30.4
```

```
 2160 28.3   6.1   30.4
```

```
 2400 28.9   6.1   30.4
```

```
 2700 29.3   6.1   30.4
```

```
 3000 29.6   6.1   30.4
```

```
 3300 29.8   6.1   30.4
```

```
 3600 29.9   6.1   30.4
```

```
 /*
```

```
 0   8.7   8.7   44.1
```

15	9.3	8.7	44.1
30	9.9	8.7	44.1
45	10.4	8.7	44.1
60	11.0	8.7	44.1
75	11.5	8.7	44.1
90	11.9	8.7	44.1
120	12.7	8.7	44.1
150	13.6	8.7	44.1
180	14.4	8.7	44.1
210	15.1	8.7	44.1
240	15.8	8.7	44.1
270	16.5	8.7	44.1
300	17.2	8.7	44.1
330	17.9	8.7	44.1
360	18.6	8.7	44.1
390	19.2	8.7	44.1
420	20.1	8.7	44.1
450	20.8	8.7	44.1
480	21.5	8.7	44.1
510	22.2	8.7	44.1
540	23.0	8.7	44.1
570	23.8	8.7	44.1
600	24.6	8.7	44.1
630	25.5	8.7	44.1
660	26.2	8.7	44.1
690	26.9	8.7	44.1
720	27.6	8.7	44.1
750	28.3	8.7	44.1
780	28.9	8.7	44.1
810	29.5	8.7	44.1
840	30.2	8.7	44.1
900	31.2	8.7	44.1
960	32.3	8.7	44.1
1020	33.3	8.7	44.1
1080	34.2	8.7	44.1
1140	35.0	8.7	44.1
1200	35.8	8.7	44.1
1260	36.4	8.7	44.1
1320	37.1	8.7	44.1
1380	37.7	8.7	44.1
1440	38.3	8.7	44.1
1560	39.3	8.7	44.1
1680	40.1	8.7	44.1
1800	40.8	8.7	44.1
1980	41.6	8.7	44.1
2160	42.2	8.7	44.1
2400	42.8	8.7	44.1
2700	43.3	8.7	44.1
3000	43.6	8.7	44.1
3660	44.0	8.7	44.1
3960	44.1	8.7	44.1

0	23.0	23.0	63.3
15	23.5	23.0	63.3
30	23.9	23.0	63.3
45	24.4	23.0	63.3
60	25.1	23.0	63.3
75	25.8	23.0	63.3
90	26.6	23.0	63.3
105	27.6	23.0	63.3
120	28.4	23.0	63.3
135	29.2	23.0	63.3
150	29.8	23.0	63.3
165	30.6	23.0	63.3
180	31.3	23.0	63.3
195	32.0	23.0	63.3

210	32.7	23.0	63.3
225	33.3	23.0	63.3
240	34.0	23.0	63.3
255	34.7	23.0	63.3
270	35.3	23.0	63.3
300	36.6	23.0	63.3
330	37.7	23.0	63.3
360	38.9	23.0	63.3
390	40.0	23.0	63.3
420	41.1	23.0	63.3
450	42.2	23.0	63.3
480	43.1	23.0	63.3
510	44.1	23.0	63.3
540	45.1	23.0	63.3
570	45.9	23.0	63.3
600	46.7	23.0	63.3
630	47.5	23.0	63.3
660	48.3	23.0	63.3
690	49.0	23.0	63.3
720	49.7	23.0	63.3
780	51.1	23.0	63.3
840	52.3	23.0	63.3
900	53.3	23.0	63.3
960	54.3	23.0	63.3
1020	55.3	23.0	63.3
1080	56.1	23.0	63.3
1140	56.9	23.0	63.3
1200	57.6	23.0	63.3
1260	58.2	23.0	63.3
1320	58.8	23.0	63.3
1380	59.3	23.0	63.3
1500	60.1	23.0	63.3
1620	60.9	23.0	63.3
1740	61.4	23.0	63.3
1920	62.0	23.0	63.3
2100	62.5	23.0	63.3
2280	62.8	23.0	63.3
2700	63.1	23.0	63.3
2820	63.2	23.0	63.3

0	24.7	24.7	77.5
15	25.3	24.7	77.5
30	26.2	24.7	77.5
45	27.7	24.7	77.5
60	29.1	24.7	77.5
75	31.9	24.7	77.5
90	33.6	24.7	77.5
105	35.1	24.7	77.5
120	36.5	24.7	77.5
135	37.8	24.7	77.5
150	39.2	24.7	77.5
165.	40.5	24.7	77.5
180	41.6	24.7	77.5
195	42.7	24.7	77.5
210	43.7	24.7	77.5
225	44.6	24.7	77.5
240	45.4	24.7	77.5
255	46.5	24.7	77.5
270	47.3	24.7	77.5
285	48.1	24.7	77.5
300	49.0	24.7	77.5
315	49.7	24.7	77.5
330	50.4	24.7	77.5
345	51.1	24.7	77.5
360	51.9	24.7	77.5
390	52.7	24.7	77.5

420	53.7	24.7	77.5
450	54.9	24.7	77.5
480	56.0	24.7	77.5
510	57.1	24.7	77.5
540	58.0	24.7	77.5
585	59.5	24.7	77.5
600	60.0	24.7	77.5
630	60.8	24.7	77.5
660	61.6	24.7	77.5
690	62.4	24.7	77.5
720	63.2	24.7	77.5
750	64.0	24.7	77.5
780	64.7	24.7	77.5
810	65.4	24.7	77.5
840	66.1	24.7	77.5
870	66.8	24.7	77.5
900	67.4	24.7	77.5
930	68.0	24.7	77.5
960	68.6	24.7	77.5
990	69.1	24.7	77.5
1020	69.7	24.7	77.5
1050	70.2	24.7	77.5
1080	70.7	24.7	77.5
1140	71.3	24.7	77.5
1200	72.1	24.7	77.5
1260	72.6	24.7	77.5
1380	73.7	24.7	77.5
1500	74.6	24.7	77.5
1620	75.3	24.7	77.5
1740	76.0	24.7	77.5
1860	76.4	24.7	77.5
2100	77.1	24.7	77.5
2280	77.4	24.7	77.5

0	24.4	24.4	86.0
15	25.6	24.4	86.0
30	26.0	24.4	86.0
60	27.7	24.4	86.0
75	29.4	24.4	86.0
90	31.1	24.4	86.0
105	32.6	24.4	86.0
120	34.0	24.4	86.0
135	35.4	24.4	86.0
150	37.0	24.4	86.0
165	38.1	24.4	86.0
180	39.5	24.4	86.0
195	40.7	24.4	86.0
210	41.8	24.4	86.0
240	44.2	24.4	86.0
255	45.3	24.4	86.0
270	46.4	24.4	86.0
285	47.5	24.4	86.0
300	48.6	24.4	86.0
315	49.6	24.4	86.0
330	50.6	24.4	86.0
345	51.6	24.4	86.0
360	52.6	24.4	86.0
375	53.5	24.4	86.0
390	54.4	24.4	86.0
405	55.2	24.4	86.0
435	56.2	24.4	86.0
450	57.0	24.4	86.0
480	58.7	24.4	86.0
510	60.1	24.4	86.0
540	61.6	24.4	86.0
570	63.0	24.4	86.0

```

600  64.2  24.4  86.0
630  65.5  24.4  86.0
660  66.7  24.4  86.0
690  67.8  24.4  86.0
720  68.9  24.4  86.0
765  70.3  24.4  86.0
840  72.6  24.4  86.0
900  74.3  24.4  86.0
960  75.7  24.4  86.0
1020 77.1  24.4  86.0
1080 78.3  24.4  86.0
1140 79.4  24.4  86.0
1200 80.4  24.4  86.0
1320 81.9  24.4  86.0
1440 83.1  24.4  86.0
1620 84.4  24.4  86.0
1800 85.1  24.4  86.0
1980 85.7  24.4  86.0
2160 85.9  24.4  86.0

*/
run;

data dim;
  set ht;

  theta=(T-Ts) / (To-Ts) ;

run;

proc nlin data=dim converge=0.0000000001;
  parm alpha=0.001;

  model theta=2*(exp(-n0**2*alpha*ti/L**2)/n0
    -exp(-n1**2*alpha*ti/L**2)/n1
    +exp(-n2**2*alpha*ti/L**2)/n2
    -exp(-n3**2*alpha*ti/L**2)/n3
    +exp(-n4**2*alpha*ti/L**2)/n4
    -exp(-n5**2*alpha*ti/L**2)/n5
    +exp(-n6**2*alpha*ti/L**2)/n6
    -exp(-n7**2*alpha*ti/L**2)/n7);

  /*
  der.alpha=2*(exp(-n0**2*alpha*ti/L**2)/n0*(-n0**2*alpha/L**2)
    -exp(-n1**2*alpha*ti/L**2)/n1*(-n1**2*alpha/L**2)
    +exp(-n2**2*alpha*ti/L**2)/n2*(-n2**2*alpha/L**2)
    -exp(-n3**2*alpha*ti/L**2)/n3*(-n3**2*alpha/L**2)
    +exp(-n4**2*alpha*ti/L**2)/n4*(-n4**2*alpha/L**2)
    -exp(-n5**2*alpha*ti/L**2)/n5*(-n5**2*alpha/L**2)
    +exp(-n6**2*alpha*ti/L**2)/n6*(-n6**2*alpha/L**2)
    -exp(-n7**2*alpha*ti/L**2)/n7*(-n7**2*alpha/L**2));
  */

run;

```

```
title 'Thermal Diffusivity for CCSM';
```

```
data ht;
```

```
n0=3.1415926/2;
```

```
n1=3*n0;
```

```
n2=5*n0;
```

```
n3=7*n0;
```

```
n4=9*n0;
```

```
n5=11*n0;
```

```
n6=13*n0;
```

```
n7=15*n0;
```

```
L=1.3;
```

```
input ti T To Ts;
```

```
cards;
```

```
0     8.7   8.7   30.4
```

```
15    8.8   8.7   30.4
```

```
30    8.9   8.7   30.4
```

```
45    9.0   8.7   30.4
```

```
60    9.2   8.7   30.4
```

```
90    9.4   8.7   30.4
```

```
120   9.7   8.7   30.4
```

```
150   10.1  8.7   30.4
```

```
180   10.5  8.7   30.4
```

```
210   11.2  8.7   30.4
```

```
240   11.9  8.7   30.4
```

```
270   12.5  8.7   30.4
```

```
300   13.1  8.7   30.4
```

```
330   13.7  8.7   30.4
```

```
360   14.3  8.7   30.4
```

```
390   14.9  8.7   30.4
```

```
420   15.5  8.7   30.4
```

```
450   16.1  8.7   30.4
```

```
480   16.6  8.7   30.4
```

```
510   17.1  8.7   30.4
```

```
540   17.6  8.7   30.4
```

```
570   18.2  8.7   30.4
```

```
600   18.7  8.7   30.4
```

```
630   19.1  8.7   30.4
```

```
660   19.5  8.7   30.4
```

```
690   20.0  8.7   30.4
```

```
720   20.5  8.7   30.4
```

```
750   20.9  8.7   30.4
```

```
780   21.3  8.7   30.4
```

```
840   22.1  8.7   30.4
```

```
900   22.8  8.7   30.4
```

```
960   23.4  8.7   30.4
```

```
1020  24.0  8.7   30.4
```

```
1080  24.5  8.7   30.4
```

```
1200  25.6  8.7   30.4
```

```
1320  26.4  8.7   30.4
```

```
1440  27.1  8.7   30.4
```

```
1560  27.6  8.7   30.4
```

```
1680  28.1  8.7   30.4
```

```
1860  28.6  8.7   30.4
```

```
2100  29.2  8.7   30.4
```

```
2400  29.6  8.7   30.4
```

```
2700  29.9  8.7   30.4
```

```
3000  30.1  8.7   30.4
```

```
3300  30.2  8.7   30.4
```

```
3600  30.3  8.7   30.4
```

```
/*
```

```
0     8.1   8.1   44.2
```

15	8.3	8.1	44.2
30	8.4	8.1	44.2
60	8.9	8.1	44.2
90	9.7	8.1	44.2
120	10.7	8.1	44.2
150	11.8	8.1	44.2
180	12.9	8.1	44.2
210	14.0	8.1	44.2
240	15.1	8.1	44.2
270	16.2	8.1	44.2
300	17.3	8.1	44.2
330	18.4	8.1	44.2
360	19.5	8.1	44.2
390	20.6	8.1	44.2
420	21.6	8.1	44.2
450	22.6	8.1	44.2
480	23.6	8.1	44.2
510	24.5	8.1	44.2
540	25.5	8.1	44.2
570	26.5	8.1	44.2
600	27.3	8.1	44.2
630	28.1	8.1	44.2
660	28.9	8.1	44.2
690	29.6	8.1	44.2
720	30.3	8.1	44.2
780	31.5	8.1	44.2
840	32.7	8.1	44.2
900	33.8	8.1	44.2
960	34.8	8.1	44.2
1020	35.7	8.1	44.2
1080	36.5	8.1	44.2
1140	37.2	8.1	44.2
1200	37.8	8.1	44.2
1260	38.5	8.1	44.2
1380	39.5	8.1	44.2
1560	40.6	8.1	44.2
1680	41.3	8.1	44.2
1800	41.8	8.1	44.2
1980	42.4	8.1	44.2
2160	42.8	8.1	44.2
2400	43.2	8.1	44.2
2700	43.6	8.1	44.2
3000	43.8	8.1	44.2
3300	44.0	8.1	44.2
3600	44.1	8.1	44.2

0	22.2	22.2	63.6
15	22.6	22.2	63.6
30	22.8	22.2	63.6
45	23.1	22.2	63.6
60	23.6	22.2	63.6
90	24.9	22.2	63.6
120	26.6	22.2	63.6
135	27.5	22.2	63.6
150	28.3	22.2	63.6
180	30.0	22.2	63.6
210	31.8	22.2	63.6
225	32.5	22.2	63.6
240	33.4	22.2	63.6
255	34.2	22.2	63.6
270	35.0	22.2	63.6
285	35.8	22.2	63.6
300	36.7	22.2	63.6
315	37.3	22.2	63.6
330	38.1	22.2	63.6

345	38.9	22.2	63.6
360	39.5	22.2	63.6
375	40.3	22.2	63.6
390	41.0	22.2	63.6
405	41.7	22.2	63.6
420	42.4	22.2	63.6
435	42.9	22.2	63.6
450	43.6	22.2	63.6
465	44.1	22.2	63.6
480	44.6	22.2	63.6
510	45.7	22.2	63.6
540	46.8	22.2	63.6
570	47.8	22.2	63.6
600	48.7	22.2	63.6
630	49.5	22.2	63.6
660	50.4	22.2	63.6
690	51.1	22.2	63.6
720	51.8	22.2	63.6
750	52.5	22.2	63.6
780	53.2	22.2	63.6
810	53.8	22.2	63.6
840	54.4	22.2	63.6
870	54.8	22.2	63.6
900	55.5	22.2	63.6
930	56.0	22.2	63.6
960	56.5	22.2	63.6
1020	57.3	22.2	63.6
1080	57.9	22.2	63.6
1140	58.7	22.2	63.6
1200	59.3	22.2	63.6
1260	59.8	22.2	63.6
1320	60.0	22.2	63.6
1440	60.7	22.2	63.6
1620	61.6	22.2	63.6
1800	62.1	22.2	63.6
2040	62.7	22.2	63.6
2280	63.0	22.2	63.6
2520	63.2	22.2	63.6

0	24.3	24.3	77.9
15	25.3	24.3	77.9
30	25.7	24.3	77.9
45	26.1	24.3	77.9
60	26.8	24.3	77.9
75	27.7	24.3	77.9
90	28.8	24.3	77.9
104	30.0	24.3	77.9
120	31.1	24.3	77.9
135	32.3	24.3	77.9
150	33.6	24.3	77.9
165	34.7	24.3	77.9
180	35.9	24.3	77.9
195	37.2	24.3	77.9
210	38.4	24.3	77.9
225	39.7	24.3	77.9
240	40.9	24.3	77.9
255	42.0	24.3	77.9
270	43.3	24.3	77.9
285	44.3	24.3	77.9
300	45.4	24.3	77.9
315	46.5	24.3	77.9
330	47.5	24.3	77.9
345	48.6	24.3	77.9
360	49.6	24.3	77.9
375	50.6	24.3	77.9

390	51.5	24.3	77.9
405	52.5	24.3	77.9
420	53.4	24.3	77.9
435	54.2	24.3	77.9
450	55.1	24.3	77.9
465	55.9	24.3	77.9
480	56.7	24.3	77.9
495	57.5	24.3	77.9
525	58.9	24.3	77.9
540	59.7	24.3	77.9
555	60.3	24.3	77.9
570	60.9	24.3	77.9
585	61.6	24.3	77.9
600	62.2	24.3	77.9
615	62.8	24.3	77.9
630	63.4	24.3	77.9
645	64.0	24.3	77.9
660	64.4	24.3	77.9
675	65.0	24.3	77.9
690	65.5	24.3	77.9
720	66.4	24.3	77.9
750	67.3	24.3	77.9
780	68.0	24.3	77.9
810	68.8	24.3	77.9
840	69.5	24.3	77.9
870	70.2	24.3	77.9
900	70.7	24.3	77.9
960	71.8	24.3	77.9
1020	72.7	24.3	77.9
1080	73.3	24.3	77.9
1155	74.2	24.3	77.9
1200	74.5	24.3	77.9
1320	75.3	24.3	77.9
1440	75.9	24.3	77.9
1560	76.4	24.3	77.9
1800	77.0	24.3	77.9
2100	77.3	24.3	77.9

0	23.8	23.8	86.5
15	24.4	23.8	86.5
30	24.8	23.8	86.5
60	25.9	23.8	86.5
75	26.8	23.8	86.5
90	28.0	23.8	86.5
105	29.3	23.8	86.5
120	30.5	23.8	86.5
135	32.0	23.8	86.5
150	33.3	23.8	86.5
165	34.9	23.8	86.5
180	36.5	23.8	86.5
195	37.7	23.8	86.5
210	39.4	23.8	86.5
225	40.8	23.8	86.5
240	42.4	23.8	86.5
255	43.8	23.8	86.5
270	45.3	23.8	86.5
285	46.6	23.8	86.5
300	47.9	23.8	86.5
315	49.3	23.8	86.5
330	50.6	23.8	86.5
345	52.0	23.8	86.5
360	53.2	23.8	86.5
375	54.4	23.8	86.5
390	55.6	23.8	86.5
405	56.7	23.8	86.5

```

420  57.8  23.8  86.5
435  58.8  23.8  86.5
450  59.8  23.8  86.5
465  60.9  23.8  86.5
480  61.9  23.8  86.5
510  63.6  23.8  86.5
540  65.5  23.8  86.5
570  67.1  23.8  86.5
600  68.7  23.8  86.5
630  69.9  23.8  86.5
660  71.4  23.8  86.5
690  72.6  23.8  86.5
720  73.7  23.8  86.5
750  74.8  23.8  86.5
780  75.7  23.8  86.5
810  76.6  23.8  86.5
840  77.5  23.8  86.5
870  78.2  23.8  86.5
900  78.9  23.8  86.5
960  80.2  23.8  86.5
1020 81.1  23.8  86.5
1080 82.0  23.8  86.5
1200 83.4  23.8  86.5
1380 84.7  23.8  86.5
1560 85.5  23.8  86.5
1800 86.2  23.8  86.5
2040 86.5  23.8  86.5

```

*/

run;

```

data dim;
  set ht;
  theta=(T-Ts) / (To-Ts);

```

run;

proc nlin data=dim converge=0.0000000001;

parm alpha=0.001;

```

  model theta=2*(exp(-n0**2*alpha*ti/L**2)/n0
    -exp(-n1**2*alpha*ti/L**2)/n1
    +exp(-n2**2*alpha*ti/L**2)/n2
    -exp(-n3**2*alpha*ti/L**2)/n3
    +exp(-n4**2*alpha*ti/L**2)/n4
    -exp(-n5**2*alpha*ti/L**2)/n5
    +exp(-n6**2*alpha*ti/L**2)/n6
    -exp(-n7**2*alpha*ti/L**2)/n7);

```

/*

```

  der.alpha=2*(exp(-n0**2*alpha*ti/L**2)/n0*(-n0**2*alpha/L**2)
    -exp(-n1**2*alpha*ti/L**2)/n1*(-n1**2*alpha/L**2)
    +exp(-n2**2*alpha*ti/L**2)/n2*(-n2**2*alpha/L**2)
    -exp(-n3**2*alpha*ti/L**2)/n3*(-n3**2*alpha/L**2)
    +exp(-n4**2*alpha*ti/L**2)/n4*(-n4**2*alpha/L**2)
    -exp(-n5**2*alpha*ti/L**2)/n5*(-n5**2*alpha/L**2)
    +exp(-n6**2*alpha*ti/L**2)/n6*(-n6**2*alpha/L**2)
    -exp(-n7**2*alpha*ti/L**2)/n7*(-n7**2*alpha/L**2));

```

*/
run;

Appendix 8.

Modeling Results of Determination of Thermal Diffusivities of Biomass Feedstocks

Thermal Diffusivity for Hybrid Poplar Bark at 30.5
11:36 Monday, August 15, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 0.412136
-1 0.001100 0.257988
0 0.001100 0.257988
1 0.001232 0.174039
2 0.001260 0.169874
3 0.001271 0.169373
4 0.001273 0.169347
5 0.001274 0.169345
6 0.001274 0.169345
7 0.001274 0.169345

Thermal Diffusivity for Hybrid Poplar Bark 25
11:36 Monday, August 15, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
8 0.001274 0.169345
9 0.001274 0.169345
10 0.001274 0.169345

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 13.691038831 13.691038831
Residual 46 0.169344863 0.003681410
Uncorrected Total 47 13.860383694

(Corrected Total) 46 4.646464189

Thermal Diffusivity for Hybrid Poplar Bark 26
11:36 Monday, August 15, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0012742712	0.00003634715	0.00120110837 0.00134743396

Asymptotic Correlation Matrix

Corr	ALPHA
ALPHA	1

Thermal Diffusivity for Hybrid Poplar Bark at 44.2 C
11:36 Monday, August 15, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA

DUD	ALPHA	Sum of Squares
-2	0.001000	0.633447
-1	0.001100	0.394584
0	0.001100	0.394584
1	0.001323	0.154294
2	0.001376	0.140723
3	0.001399	0.138904
4	0.001404	0.138805
5	0.001405	0.138796
6	0.001406	0.138795
7	0.001406	0.138795

Thermal Diffusivity for Hybrid Poplar Bark 28
11:36 Monday, August 15, 1994

Non-Linear Least Squares Iterative Phase

Dependent Variable THETA	Method: DUD
Iter	ALPHA Sum of Squares
8	0.001406
9	0.001406
10	0.001406
11	0.001406

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA

Source	DF	Sum of Squares	Mean Square
Regression	1	15.108572099	15.108572099
Residual	47	0.138795080	0.002953087
Uncorrected Total	48	15.247367178	
(Corrected Total)	47	4.786759853	

Thermal Diffusivity for Hybrid Poplar Bark 29
11:36 Monday, August 15, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0014060292	0.00003527440	0.00133506649 0.00147699200

Asymptotic Correlation Matrix

Corr	ALPHA
-----	-----
ALPHA	1

Thermal Diffusivity for Hybrid Poplar Bark at 63.5 C
11:36 Monday, August 15, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA

DUD	ALPHA	Sum of Squares
-2	0.001000	2.081217
-1	0.001100	1.618113
0	0.001100	1.618113
1	0.001572	0.513953
2	0.001740	0.395263
3	0.001843	0.367280
4	0.001876	0.364331
5	0.001890	0.363898
6	0.001894	0.363852
7	0.001896	0.363846

Thermal Diffusivity for Hybrid Poplar Bark 45
11:36 Monday, August 15, 1994

Non-Linear Least Squares Iterative Phase

Dependent Variable THETA	Method: DUD
Iter	ALPHA Sum of Squares
8	0.001896
9	0.363845
10	0.001897
11	0.363845
12	0.001897
13	0.363845

NOTE: Convergence criterion met.

Thermal Diffusivity for Hybrid Poplar Bark 46
11:36 Monday, August 15, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable THETA

Source	DF	Sum of Squares	Mean Square
Regression	1	13.489661082	13.489661082
Residual	48	0.363845020	0.007580105
Uncorrected Total	49	13.853506101	
(Corrected Total)	48	3.809967575	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
ALPHA	0.0018966312	0.00007311227	Lower Upper

0.00174962945 0.00204363286
Thermal Diffusivity for Hybrid Poplar Bark 47
11:36 Monday, August 15, 1994

Asymptotic Correlation Matrix

Corr ALPHA

ALPHA 1

Thermal Diffusivity for Hybrid Poplar Bark at 77.4 C
11:36 Monday, August 15, 1994

Non-Linear Least Squares DUD Initialization

DUD	ALPHA	Sum of Squares
-2	0.001000	2.751246
-1	0.001100	2.121835
0	0.001100	2.121835
1	0.001624	0.521668
2	0.001832	0.341249
3	0.001958	0.301746
4	0.001998	0.297855
5	0.002013	0.297364
6	0.002018	0.297317
7	0.002019	0.297312

Thermal Diffusivity for Hybrid Poplar Bark 35
11:36 Monday, August 15, 1994

Non-Linear Least Squares Iterative Phase

Dependent Variable THETA Method: DUD

Iter	ALPHA	Sum of Squares
8	0.002020	0.297311
9	0.002020	0.297311
10	0.002020	0.297311
11	0.002020	0.297311
12	0.002020	0.297311
13	0.002020	0.297311

NOTE: Convergence criterion met.

Thermal Diffusivity for Hybrid Poplar Bark 36
11:36 Monday, August 15, 1994

Non-Linear Least Squares Summary Statistics

Source	DF	Sum of Squares	Mean Square
Regression	1	13.063145075	13.063145075
Residual	53	0.297310941	0.005609640
Uncorrected Total	54	13.360456016	
(Corrected Total)	53	4.521329451	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper

ALPHA 0.0020200651 0.00006537824 0.00188893309 0.00215119705

Thermal Diffusivity for Hybrid Poplar Bark 37
11:36 Monday, August 15, 1994

Asymptotic Correlation Matrix

Corr ALPHA

ALPHA 1

Thermal Diffusivity for Hybrid Poplar Bark at 86.0 C
11:36 Monday, August 15, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA

DUD	ALPHA	Sum of Squares
-2	0.001000	3.367821
-1	0.001100	2.655715
0	0.001100	2.655715
1	0.001785	0.337410
2	0.002062	0.106180
3	0.002208	0.070513
4	0.002241	0.068791
5	0.002249	0.068701
6	0.002250	0.068697
7	0.002251	0.068697

Thermal Diffusivity for Hybrid Poplar Bark 39
11:36 Monday, August 15, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD

Iter	ALPHA	Sum of Squares
8	0.002251	0.068697
9	0.002251	0.068697
10	0.002251	0.068697
11	0.002251	0.068697

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA

Source	DF	Sum of Squares	Mean Square
Regression	1	13.213395890	13.213395890
Residual	48	0.068697259	0.001431193
Uncorrected Total	49	13.282093149	

(Corrected Total) 48 4.669021850

Thermal Diffusivity for Hybrid Poplar Bark 40
11:36 Monday, August 15, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0022507802	0.00003733669	0.00217570993 0.00232585045

Asymptotic Correlation Matrix

Corr	ALPHA

ALPHA	1

hermal Diffusivity for Switchgrass at 30.4 C 1
15:04 Sunday, September 11, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 0.109598
-1 0.001100 0.236855

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
0 0.001000 0.109598
1 0.000910 0.067557
2 0.000910 0.067557
3 0.000910 0.067557

NOTE: Convergence criterion met.

hermal Diffusivity for Switchgrass at 30.4 C 2
15:04 Sunday, September 11, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 17.614012774 17.614012774
Residual 45 0.067556770 0.001501262
Uncorrected Total 46 17.681569544

(Corrected Total) 45 4.343950529

Parameter Estimate Asymptotic Asymptotic 95 %
 Std. Error Confidence Interval
 Lower Upper
ALPHA 0.0009101728 0.00001569487 0.00087856180 0.00094178378

hermal Diffusivity for Switchgrass at 30.4 C 3
15:04 Sunday, September 11, 1994

Asymptotic Correlation Matrix

Corr	ALPHA
-----	-----
ALPHA	1

Thermal Diffusivity for Switchgrass at 44.1 4
15:04 Sunday, September 11, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 0.085075
-1 0.001100 0.139491

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
0 0.001000 0.085075
1 0.000997 0.084977
2 0.000995 0.084953
3 0.000995 0.084953

Thermal Diffusivity for Switchgrass at 44.1 5
15:04 Sunday, September 11, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
4 0.000995 0.084953
5 0.000995 0.084953
6 0.000995 0.084953

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics			Dependent Variable THETA
Source	DF	Sum of Squares	Mean Square
Regression	1	17.656269511	17.656269511
Residual	51	0.084952679	0.001665739
Uncorrected Total	52	17.741222190	
(Corrected Total)	51	5.108645191	

Thermal Diffusivity for Switchgrass at 44.1 6
15:04 Sunday, September 11, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0009953048	0.00001692263	0.00096133129 0.00102927836

Asymptotic Correlation Matrix

Corr	ALPHA
ALPHA	1

Thermal Diffusivity for Switchgrass at 44.1 4
15:04 Sunday, September 11, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 0.085075
-1 0.001100 0.139491

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
0 0.001000 0.085075
1 0.000997 0.084977
2 0.000995 0.084953
3 0.000995 0.084953

Thermal Diffusivity for Switchgrass at 44.1 5
15:04 Sunday, September 11, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
4 0.000995 0.084953
5 0.000995 0.084953
6 0.000995 0.084953

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 17.656269511 17.656269511
Residual 51 0.084952679 0.001665739
Uncorrected Total 52 17.741222190

(Corrected Total) 51 5.108645191

Thermal Diffusivity for Switchgrass at 44.1 6
15:04 Sunday, September 11, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0009953048	0.00001692263	0.00096133129 0.00102927836

Asymptotic Correlation Matrix

Corr	ALPHA
-----	-----
ALPHA	1

Thermal Diffusivity for Switchgrass at 86.0 C 14
15:04 Sunday, September 11, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA

DUD	ALPHA	Sum of Squares
-2	0.001000	1.321643
-1	0.001100	0.879427
0	0.001100	0.879427
1	0.001468	0.133374
2	0.001562	0.093450
3	0.001597	0.089614
4	0.001603	0.089490
5	0.001605	0.089483
6	0.001605	0.089482
7	0.001605	0.089482

Thermal Diffusivity for Switchgrass at 86.0 C 15
15:04 Sunday, September 11, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD

Iter	ALPHA	Sum of Squares
8	0.001605	0.089482
9	0.001605	0.089482
10	0.001605	0.089482

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA

Source	DF	Sum of Squares	Mean Square
Regression	1	16.366746965	16.366746965
Residual	50	0.089482479	0.001789650
Uncorrected Total	51	16.456229444	

(Corrected Total) 50 4.528563285

Thermal Diffusivity for Switchgrass at 86.0 C 16
15:04 Sunday, September 11, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0016049126	0.00002794834	0.00154877678 0.00166104835

Asymptotic Correlation Matrix

Corr	ALPHA

ALPHA	1

Thermal Diffusivity for CCSM at 30.4 C 13
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 0.009555
-1 0.001100 0.060517

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
0 0.001000 0.009555
1 0.000995 0.009394
2 0.000994 0.009393
3 0.000994 0.009393

Thermal Diffusivity for CCSM at 30.4 C 14
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
4 0.000994 0.009393
5 0.000994 0.009393

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 17.580595824 17.580595824
Residual 45 0.009393345 0.000208741
Uncorrected Total 46 17.589989169

(Corrected Total) 45 5.015298967

Thermal Diffusivity for CCSM at 30.4 C 15
21:34 Tuesday, October 4, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0009943497	6.36982487E-6	0.00098152026 0.00100717915

Asymptotic Correlation Matrix

Corr	ALPHA
-----	-----
ALPHA	1

Thermal Diffusivity for CCSM at 44.2 C 16
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA

DUD	ALPHA	Sum of Squares
-2	0.001000	0.118707
-1	0.001100	0.026969
0	0.001100	0.026969
1	0.001150	0.014907
2	0.001156	0.014747
3	0.001156	0.014743
4	0.001156	0.014743
5	0.001156	0.014743
6	0.001156	0.014743
7	0.001156	0.014743

NOTE: Convergence criterion met.

Thermal Diffusivity for CCSM at 44.2 C 17
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable THETA

Source	DF	Sum of Squares	Mean Square
Regression	1	14.563812656	14.563812656
Residual	45	0.014743371	0.000327630
Uncorrected Total	46	14.578556027	
(Corrected Total)	45	4.963758052	

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0011564376	9.38045292E-6	0.00113754443 0.00117533071

Thermal Diffusivity for CCSM at 44.2 C 18
21:34 Tuesday, October 4, 1994

Asymptotic Correlation Matrix

Corr	ALPHA
-----	-----
ALPHA	1

Thermal Diffusivity for CCSM at 77.9 C 19
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 0.001000 2.295509
-1 0.001100 1.559482
0 0.001100 1.559482
1 0.001548 0.092972
2 0.001667 0.023604
3 0.001701 0.019768
4 0.001704 0.019736
5 0.001704 0.019736
6 0.001704 0.019736
7 0.001704 0.019736

Thermal Diffusivity for CCSM at 77.9 C 20
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares Iterative Phase
Dependent Variable THETA Method: DUD
Iter ALPHA Sum of Squares
8 0.001704 0.019736

NOTE: Convergence criterion met.

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 18.713584649 18.713584649
Residual 62 0.019735690 0.000318318
Uncorrected Total 63 18.733320339

(Corrected Total) 62 5.688096697

Thermal Diffusivity for CCSM at 77.9 C 21
21:34 Tuesday, October 4, 1994

Parameter	Estimate	Asymptotic Std. Error	Asymptotic 95 % Confidence Interval
			Lower Upper
ALPHA	0.0017044086	0.00001083498	0.00168274973 0.00172606738

Asymptotic Correlation Matrix

Corr	ALPHA
ALPHA	1

Thermal Diffusivity for CCSM at 86.5 C 22
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares DUD Initialization Dependent Variable THETA
DUD ALPHA Sum of Squares
-2 .0.001000 1.927818
-1 0.001100 1.314129
0 0.001100 1.314129
1 0.001562 0.062547
2 0.001677 0.012220
3 0.001703 0.010508
4 0.001704 0.010506
5 0.001704 0.010506
6 0.001704 0.010506
7 0.001704 0.010506

NOTE: Convergence criterion met.

Thermal Diffusivity for CCSM at 86.5 C 23
21:34 Tuesday, October 4, 1994

Non-Linear Least Squares Summary Statistics Dependent Variable THETA
Source DF Sum of Squares Mean Square
Regression 1 17.655687222 17.655687222
Residual 53 0.010506317 0.000198232
Uncorrected Total 54 17.666193540
(Corrected Total) 53 5.271767876

Parameter Estimate Asymptotic Asymptotic 95 %
 Std. Error Confidence Interval
 Lower Upper
ALPHA 0.0017043296 9.25585496E-6 0.00168576474 0.00172289448
Thermal Diffusivity for CCSM at 86.5 C 24
21:34 Tuesday, October 4, 1994

Asymptotic Correlation Matrix

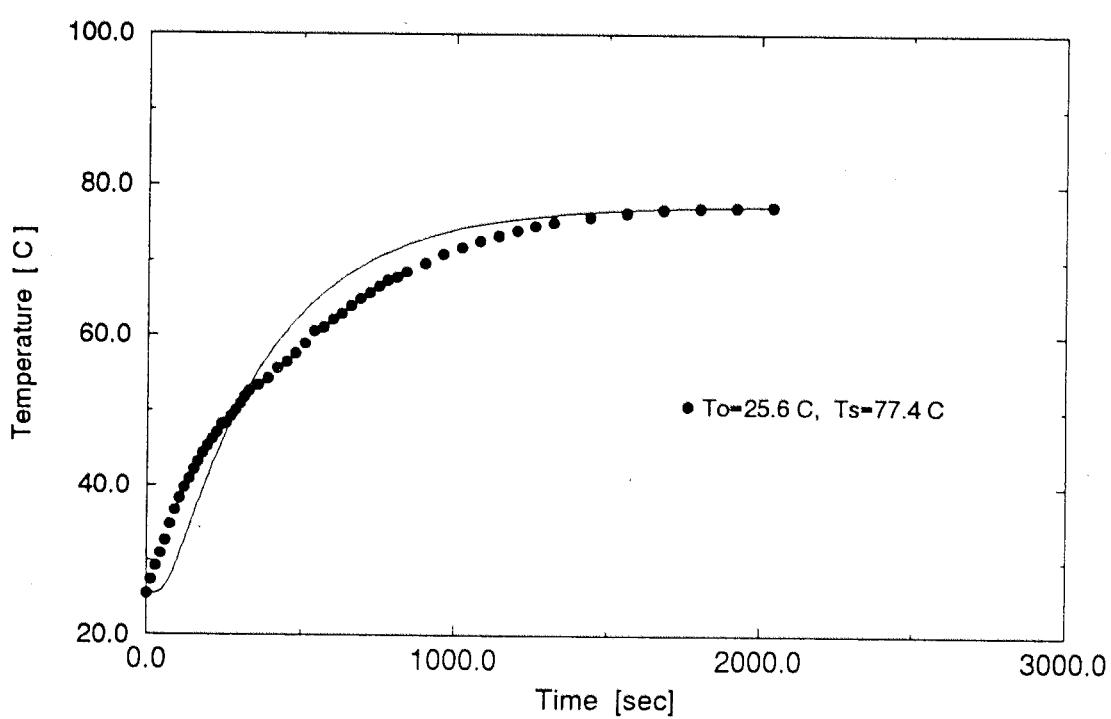
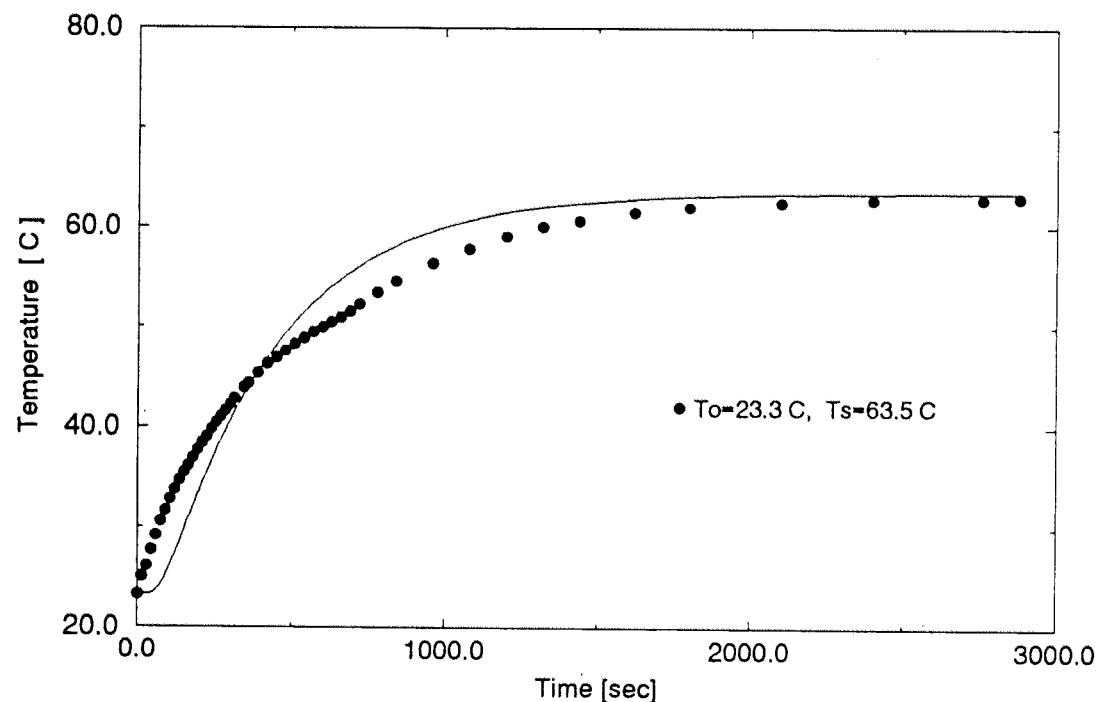
Corr	ALPHA
-----	-----
ALPHA	1

Appendix 9.

Comparison Between Experimental and Model Values

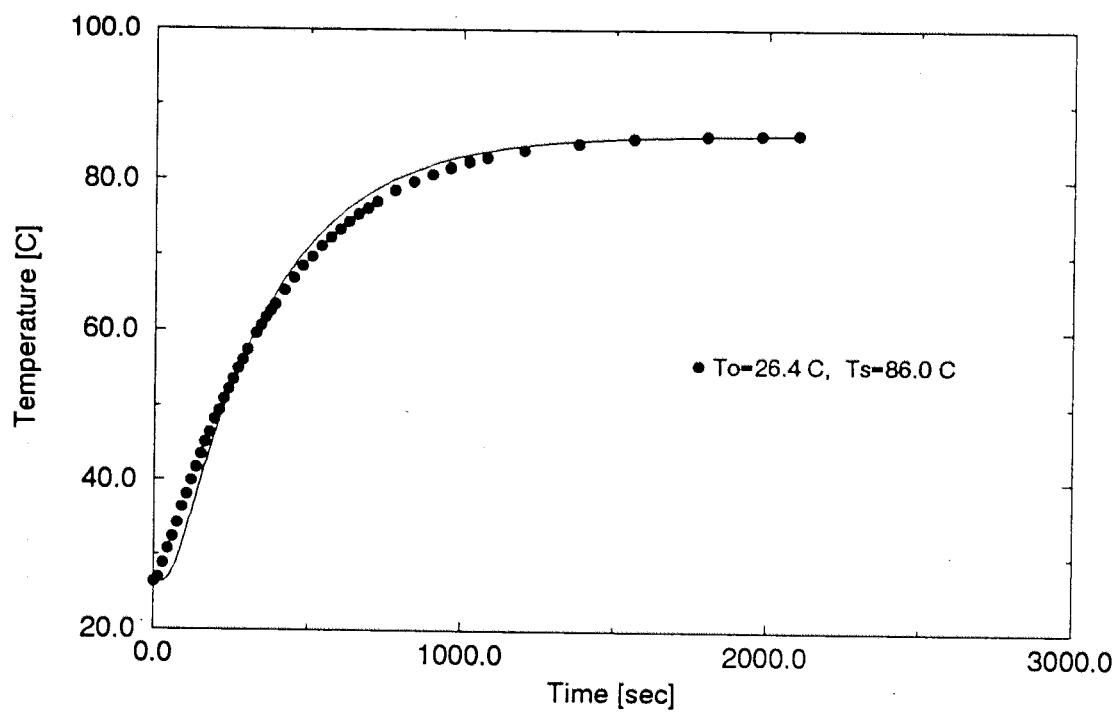
for Determination of Thermal Diffusivities of Biomass Feedstocks

Temperature Profiles at the Centers of the HPB Cell

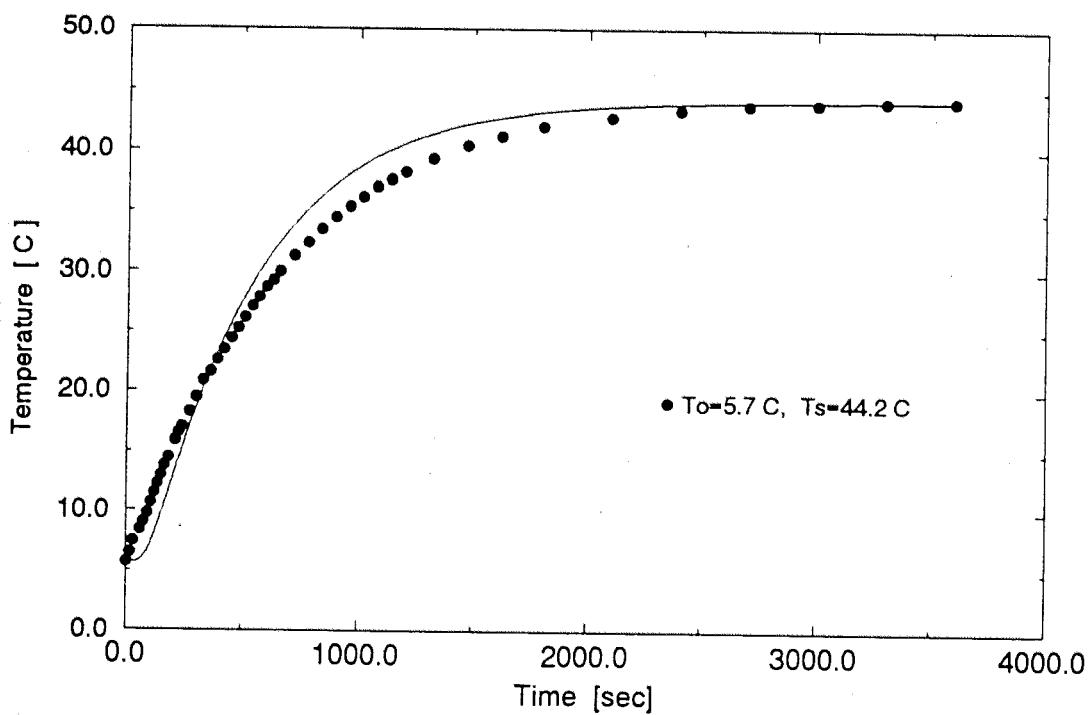
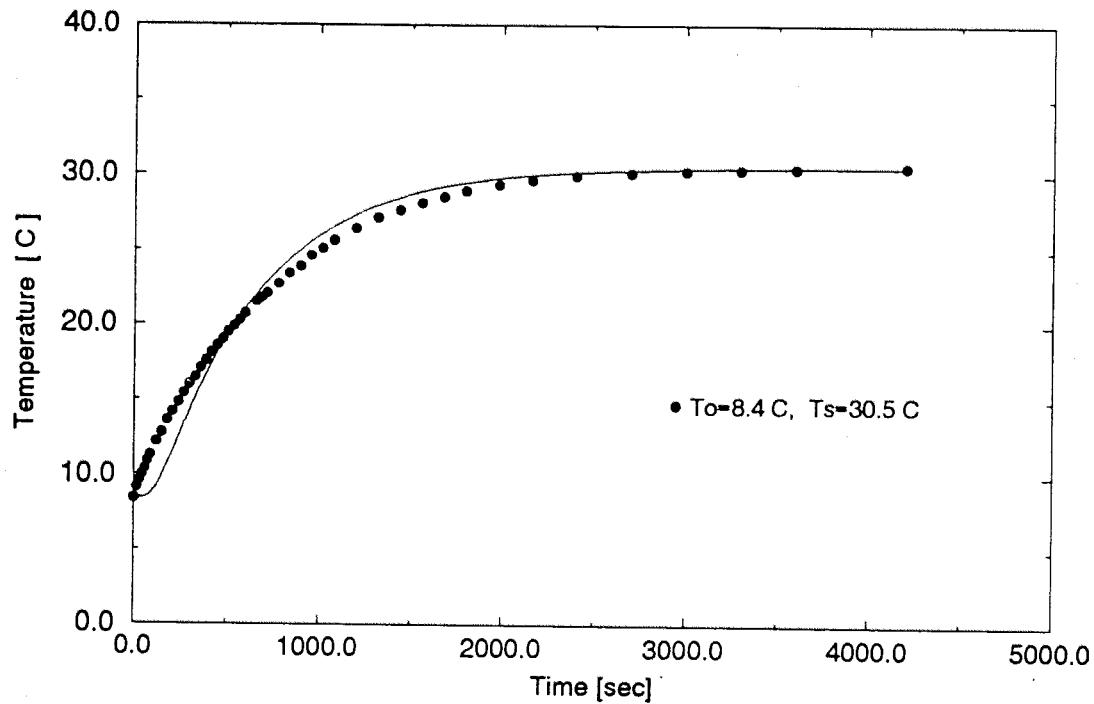


(--: Best Fit for Individual Run)

Temperature Profiles at the Centers of the HPB Cell

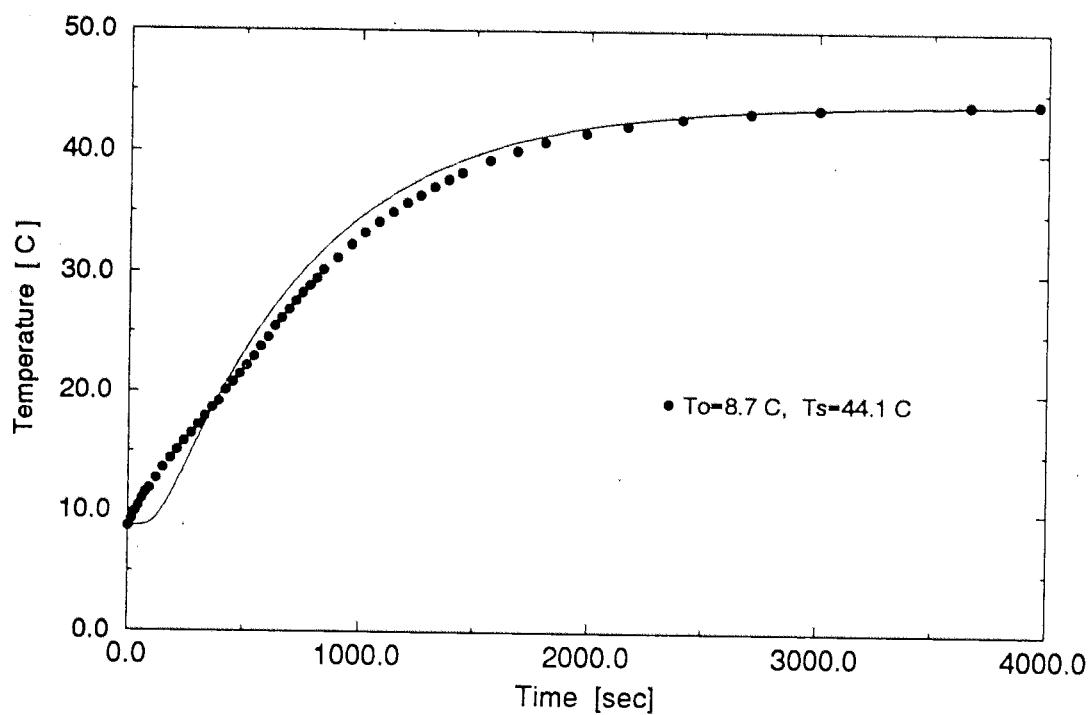
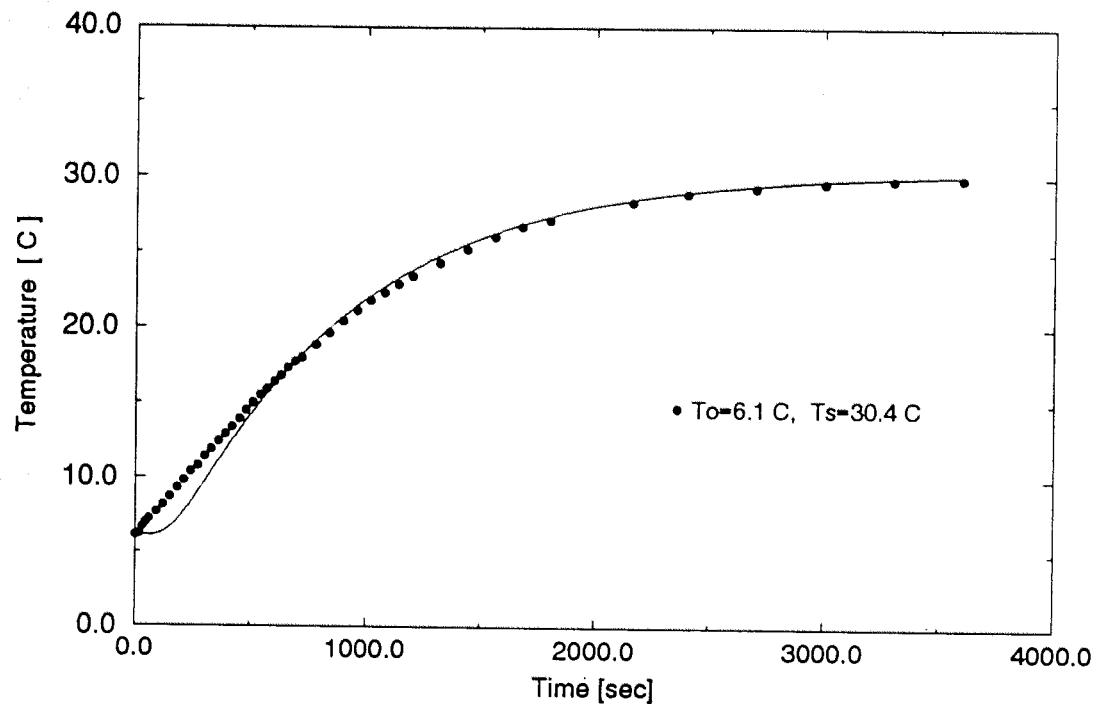


Temperature Profiles at the Centers of the HPB Cell



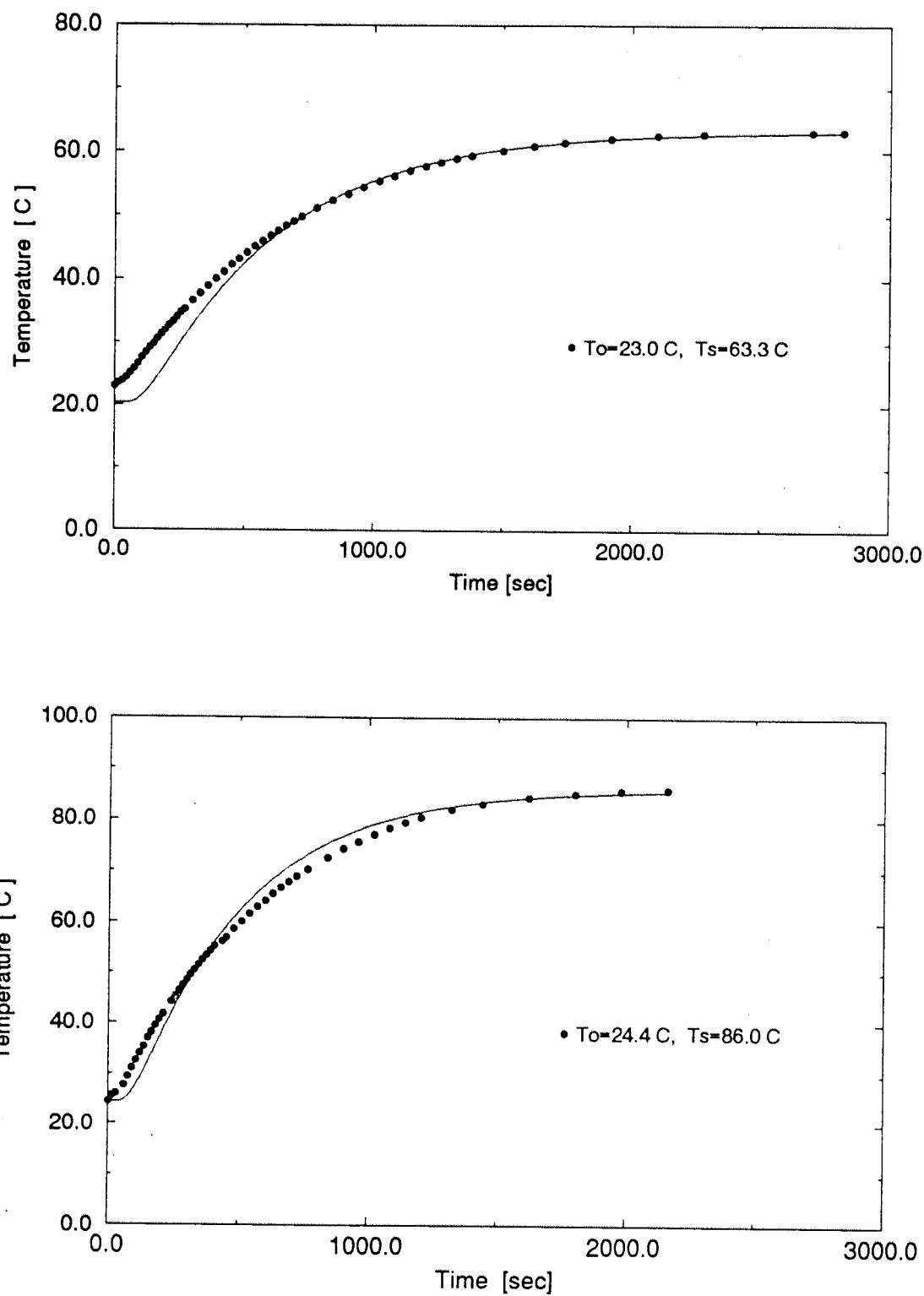
(--: Best Fit for Individual Run)

Temperature Profiles at the Centers of the SG Cell



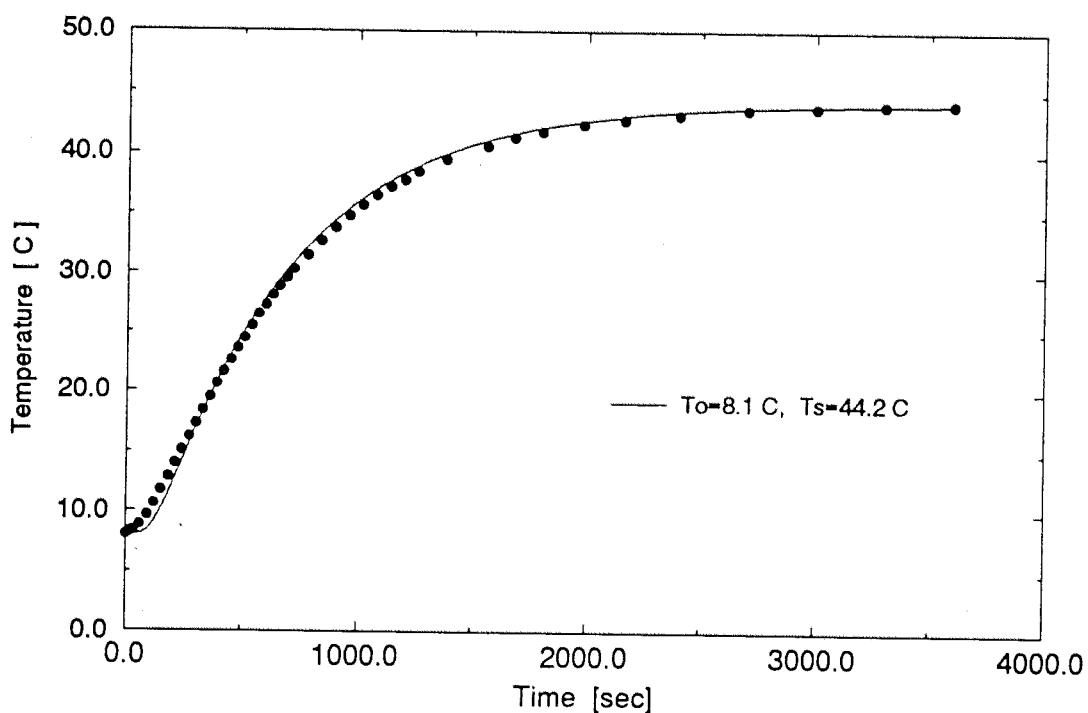
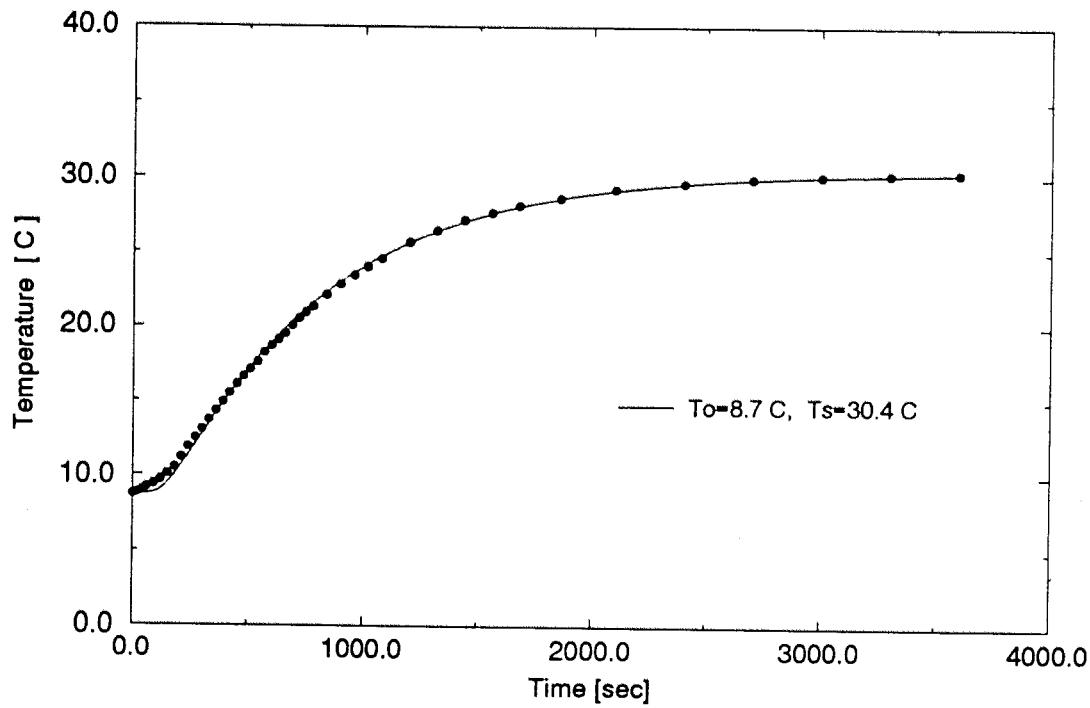
(--: Best Fit for Individual Run)

Temperature Profiles at the Centers of the SG Cell



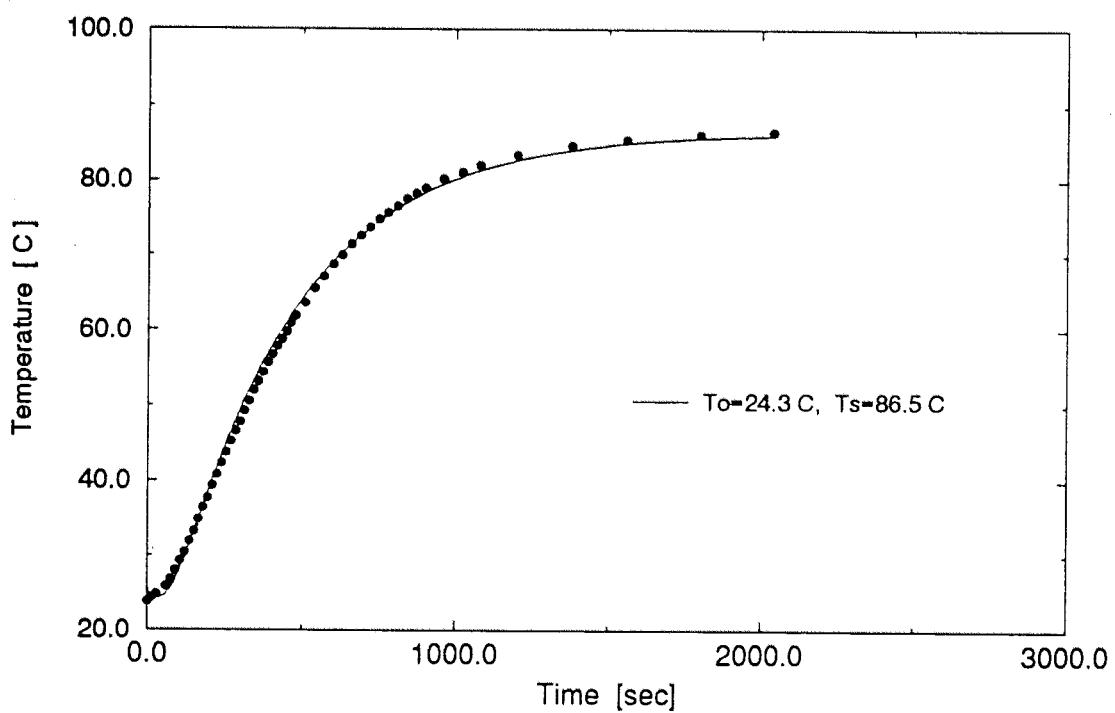
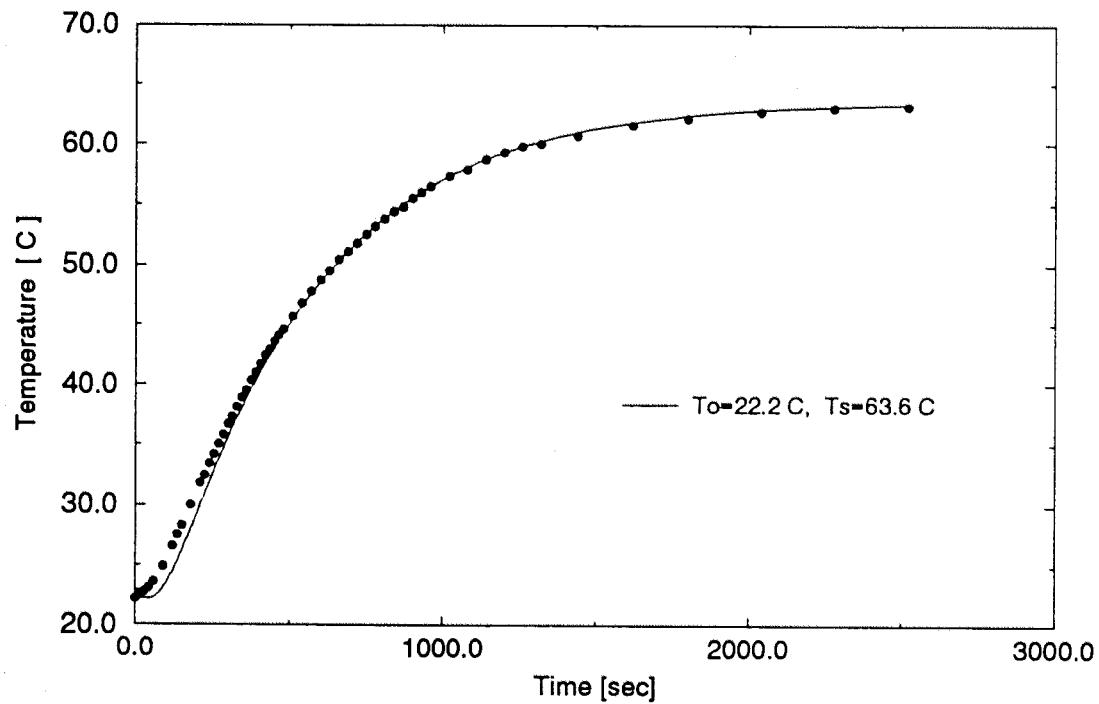
(--: Best Fit for Individual Run)

Temperature Profiles at the Centers of the CCSM Cell



(--: Best Fit for Individual Run)

Temperature Profiles at the Centers of the CCSM Cell



(--: Best Fit for Individual Run)